2004

Annulation reactions toward bicyclic and tricyclic cycloheptyne dicobalt complexes.

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Annulation Reactions Toward Bicyclic and Tricyclic Cycloheptyne Dicobalt Complexes

By

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A Thesis

Submitted to the Faculty of Graduate Studies and Research

through the Department of Chemistry and Biochemistry

in Partial Fulfillment of the Requirements for

the Degree of Master of Science at the

University of Windsor

Windsor, Ontario, Canada

2004

Your file Votre référence
ISBN: 0-612-96398-5
Our file Notre référence
ISBN: 0-612-96398-5

Abstract

Cycloheptane containing molecules widely occur in nature; however, the methods for rapid synthesis of those type compounds are limited. This thesis focused on the annulation reactions toward fused ring systems bearing a cycloheptyne dicobalt complex. A series of benzocycloheptyne dicobalt complexes **58** have been synthesized from conjugated (Z) enyne acetate dicobalt complexes **59** by intramolecular Nicholas reactions. Fused [7,6,5] system **101** has also been obtained in a one-pot reaction via [4+3] cycloaddition/intramolecular trapping reaction. In addition, the progress in intramolecular [4+2] cycloaddition of complex **80** is discussed.

Dedication

This thesis is dedicated to my parents and my wife.

Acknowledgements

First of all, my special thank goes to my supervisor James R. Green, a great mentor and brilliant scientist. His scientific intelligence and attitude has influenced and stimulated my interest in chemistry. It is his inspiration and encouragement to make my graduate studies unforgettable and full of fun.

Secondly, I would like to thank Dr. Holger Eichhorn and Dr. Brian Fryer for being my committee members. I also thank Dr. Philip Dutton and Dr. Robert Schurko for their help in the past two years.

Thirdly, I would like to thank Mr. Mike Fuerth for his friendly help in the NMR experiments. Also, I would like to thank all the professors who have taught me and the staff in our department.

Finally, I appreciated the support and help from our group members Ahmed Mohamed and Joseph DiMartino. In particular, they helped me start my project smoothly and improved my English. In addition, I thank all the students in the department for the help in the past two years

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Abbreviations

Ac	acetyl, $-C(O)CH_3$
α	alpha, one atom away from reference atom
β	beta, two atoms away from reference atom
Bn	benzyl, $-CH_2C_6H_5$
nBu	butyl, $-(CH_2)_3CH_3$
tBu	tertiary butyl, $-C(CH_3)_3$
CAN	ceric ammonium nitrate
δ	chemical shift in ppm
COD	cyclooctadiene
Cy	cyclohexyl, $-C_6H_{11}$
Cp	cyclopentadienyl, $-C_5H_5$
dba	dibenzylideneacetone
DIBAL-H	diisobutylaluminum hydride, $[(CH_3)_2CHCH_2]_2AlH$
dppe	1,2-Bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
d	doublet
dd	doublet of doublets
dt	doublet of triplets
E	electrophile
equiv.	equivalents
Et	ethyl, $-CH_2CH_3$

γ	gamma, three atoms away from reference atom
GC	gas chromatography
η	hapto
HRMS	High Resolution Mass Spectroscopy
IR	infrared
Ln	ligands
mCPBA	*meta*-chloroperoxybenzoic acid
Me	methyl, $-CH_3$
Mes	mesityl, 2,4,6–trimethylphenyl, 2,4,6–$(CH_3)_3C_6H_2$
Met	metal
Ms	mesylate, $-OSO_2CH_3$
MS	mass spectroscopy
μ	mu
mL	milliliter
mol	mole
m	multiplet
NMO	N–methylmorpholine oxide
NMR	nuclear magnetic resonance
NOE	nuclear overhauser effect
Nu	nucleophile
[O]	oxidation
OTf	triflate, $-OSO_2CF_3$
ppm	parts per million

PKR	Pauson Khand reaction
iPr	isopropyl, $-CH(CH_3)_2$
Ph	Phenyl, $-C_6H_5$
Pr	propyl, $-(CH_2)_2CH_3$
R	alkyl or aryl group
RCM	ring closing metathesis
RT	room temperature
s	singlet
TBDPS	t-butyldiphenylsilyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TIPS	triisopropylsilyl, $-Si(CH(CH_3)_2)_3$
TMS	trimethylsilyl, $-Si(CH_3)_3$
t	triplet

Introduction

The transition metal organometallic chemistry of alkynes has been investigated since the first report of Reppe on oligomeriztion of alkynes by a nickel catalyst.[1] Three types of metal coordinated alkynes are shown in the **Figure 1**; mononuclear, dinuclear, and trinuclear systems. The presence of those metals change the alkyne from a linear shape to a bent shape, ranging from 177^0 to 118.5^0 at the alkyne carbon,[2] which allow one to perform some reactions that are not possible for metal free alkynes. Among those transition-metal-complexed systems, dicobalt hexacarbonyl based ones have been used most commonly as a C-C triple bond protecting groups due to its advantages, such as stability, easy preparation and removal.

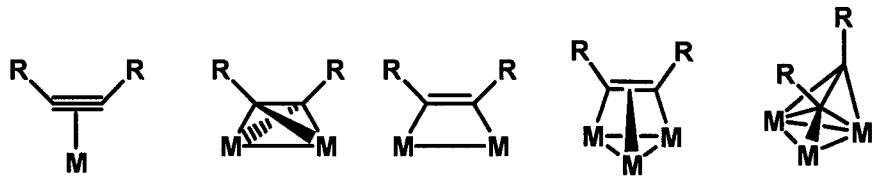


Figure 1 Transition metal coordinated alkyne

The complexation of alkynes by hexacarbonyldicobalt reduces the bond order from triple to approximately that of a double bond, with a corresponding change in bond angles, from 180^0 to 140^0 (**1** in **Figure 2**). Therefore, substituents on the end of the alkyne unit are in a much more favorable orientation for many cyclization reactions.

The complexes can be freed from the $Co_2(CO)_6$ in numerous ways, either oxidatively to form the corresponding alkynes, or reductively to form alkenes. Ceric ammonium nitrate (CAN), trimethylamine N-oxide, N-methylmorphine N-

oxide (NMO), and chloroanil have been commonly used as the oxidative reagent, while lithium, tributyltin hydride, triethylsilane have been used as reducing reagents.[3]

1. Nicholas Reaction

The Nicholas reaction, which is the chemistry of hexacarbonyl (μ-propargyllium) dicobalt cations, has been known since 1972.[4] Many research groups have applied this reaction in organic or natural product syntheses since its initial discovery.

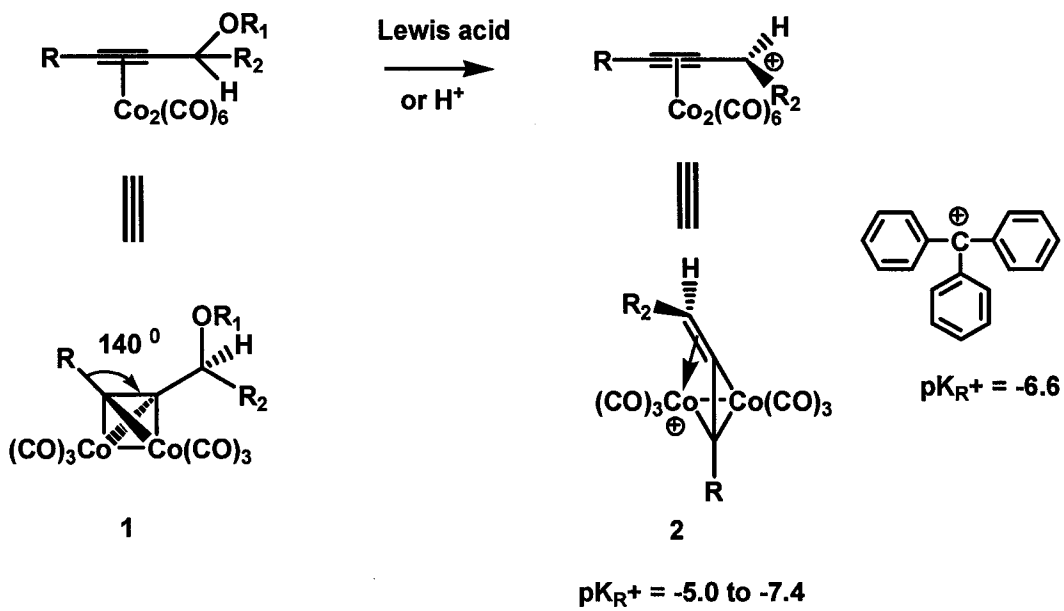


Figure 2 Structure of alkyne hexacarbonyl dicobalt complexs

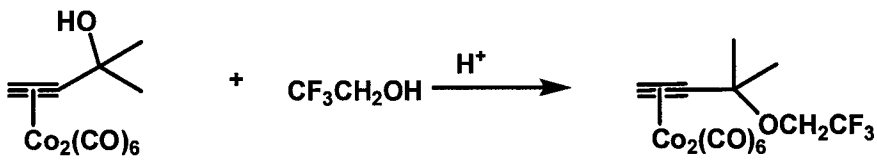
The cations (**2**) are thermodynamically stable, with pK_R+ values ranging from –5.5 to –7.0 (pK_R+ of trityl cation is -6.6).[5,6] The stability comes from the delocalization of the cation onto the cobalt atoms.[7,8] The accepted structure of propargylcobalt complexes was proposed by Schreiber [9] The cation is more like an alkene complex, with much of the positive charge residing on the metal, so

that the formal C(alkyne)-C(cation) bond is bent towards one of the cobalt atoms. Recently, Melikyan et al have proven the structure by the first X-ray crystal structure of a $Co_2(CO)_6$ complexed propargyl cation.[10] Mayr et al [11] have carefully evaluated the electrophilicity of those complexes in their reactions with several nucleophiles and their propensity for reaction with an untested nucleophile.

The cations (**2**) can be generated from complexed propargyl alcohols, ethers, and esters by treatment with protic acids or Lewis acids. Related to this method of carbocation generation is the reaction between silver tetrafluoroborate and a suitable propargyl chloride complex.[12] Those cations can be isolated in pure form, usually by precipitation as tetrafluoroborates, but are most commonly used in *situ* or directly.

1.1 Intermolecular Nicholas Reactions

The reactions of propargyl $Co_2(CO)_6^+$ complexes have been found to occur with a wide variety of nucleophiles since the first Nicholas reaction (**Figure 3**).[13] The nucleophilic substitutions of those cations are highly predictable, taking place at the propargyl site exclusively. Allene formation without prior loss of the $Co_2(CO)_6$ unit has never been reported.[14-16]



3 4

Figure 3 The first Nicholas reaction

Oxygen centered nucleophiles, such as water and alcohols, and nitrogen-based nucleophiles, including amines and sulfonamides, are capable of undergoing these reactions. Thiols are also used as nucleophiles. Among carbon based nucleophiles, enol derivatives (silyl enol ethers, silyl ketene acetals, enol borinates) and allylmetals (allylsilane, allyltrimethylborinates) are commonly used. Electron rich arenes including heterocycles will react with those complexes; benzene itself is not nucleophillic enough to react efficiently unless it is present as solvent.

1.2 Intramolecular Nicholas reactions

Several research groups have been focused on both normal (5,6) and medium size ring formation by intramolecular cyclization of cobalt stabilized propargyl cations.

The use of heteroatoms to cyclize onto these cations has provided a rapid route for the synthesis of several heterocycles. Martin, for example, has treated dicobalt protected diols **5** with a Lewis acid, causing the terminal alcohol group to cyclize onto the propargyl cation to give 7 to 9 membered cyclic ethers, which were then decomplexed by CAN to form compound **6** (**Figure 4**). [17]

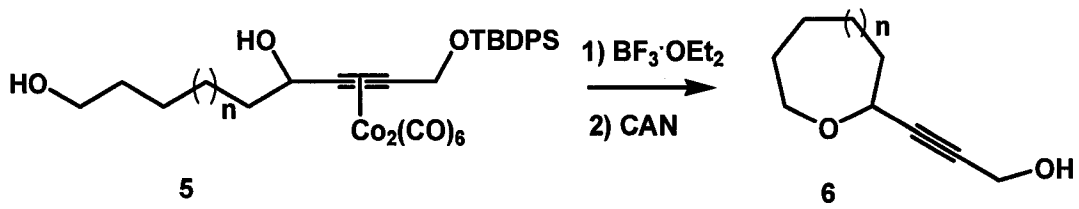


Figure 4 Cyclic ether formation

Mukai and his coworkers have reported the synthesis of tetrahydrofurans and tetrahydropyrans by reaction of $Co_2(CO)_6$ protected alkynyl epoxides with a pendant hydroxyl group (**Figure 5**).[18-20] $BF_3{\cdot}OEt_2$ opened the epoxide (**7**) to generate a propargyl cation, which in turn underwent attack by the OH group to form a substituted tetrahydropyran(**8** or **9**). Tetrahydrofuran formation occurred analogously in the one carbon shorter substrates. The reaction was highly stereoselective in that the *trans* epoxide gave predominantly the *cis* tetrahydropyran, while the *cis* epoxide favored *trans* isomer formation.

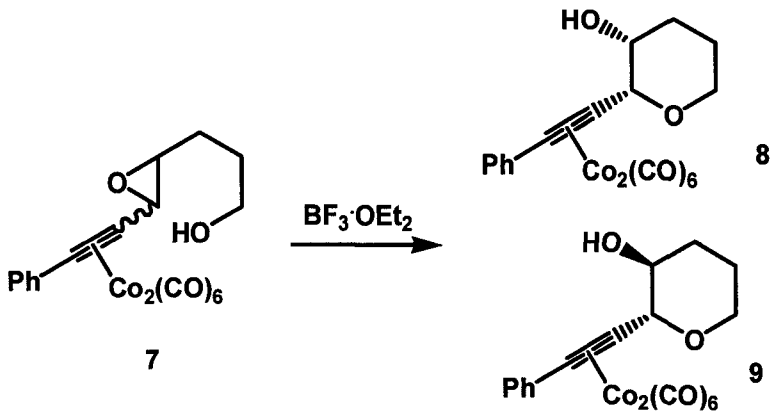


Figure 5 Intramolecular Nicholas reaction of epoxides

Grove's group has utilized electron rich arenes to cyclize onto the cation (**Figure 6**).[21,22] Reaction of alcohol **10** with $BF_3.OEt_2$ in CH_2Cl_2 at 0^0C and then immediate decomplexation by using CAN or $Fe(NO_3)_3$, gave a 72% yield of compounds **11** and **12** in a 85:15 ratio, each as a single stereoisomer. Muehldorf's [23] and Kocienski's groups[24] have reported similar cyclization reactions.

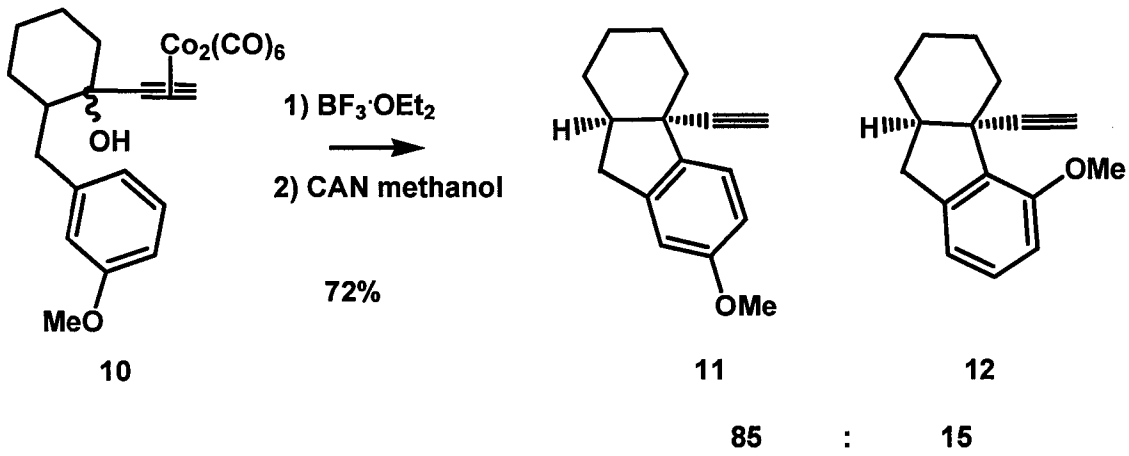


Figure 6 Intramolecular arene attack

1.3 Medium Sized Cycloalkyne Complex Formation by Nicholas Reaction

The change in bond angle of the alkyne groups by the dicobalt moiety have made it possible to form medium sized cycloalkyne complexes, often when the cycloalkynes themselves are impossible.

Schreiber and coworkers were the first to report medium sized cycloalkyne complexes formation by way of intramolecular alkylation of a propargyl cation complex with the alkyne situated between the cation and nucleophile (**Figure 7**).[25] Under Lewis acidic conditions, the allylsilane moiety of **13** cyclized onto the propargyl cation to give the cyclic alkyne complex bearing an exocyclic vinyl group. Seven, eight and even six-membered complexed cycloalkynes **14** were achieved in yields ranging from 55% to 67 %. However, attempts to obtain metal free cycloalkynes by oxidative removal of the cobalt moiety were not a success.

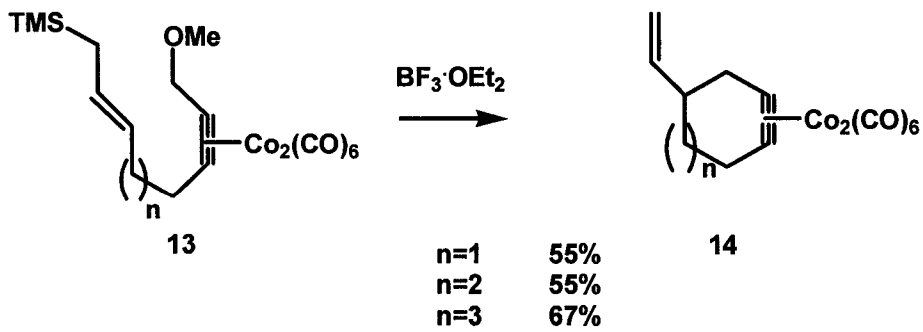
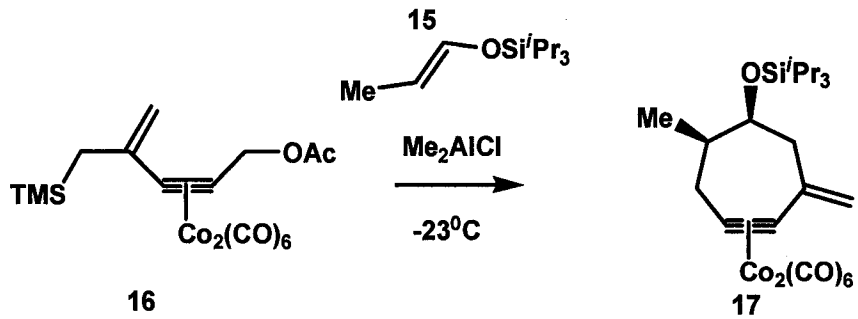


Figure 7 Intramolecular Nicholas reactions to give cycloalkyne complexes

Tanino's group has synthesized cycloheptyne complex derivatives by a [5+2] cycloaddition (**Figure 8**) that involves two separate propargylium dicobalt intermidates.[26] The cycloaddition of cyclic enol silyl ethers as well as acyclic enol silyl ethers (**15**) with complexes of type **16** have exhibited remarkably high diastereoselectivity in **17**.



84% *cis*:*trans*= 83:17

Figure 8 [5+2] Cycloaddition

Isobe's group is a major contributor to the synthesis of heterocycloalkyne complexes.[27-29] The principle of the group's work involves protic or Lewis acid mediated cyclization of a remote alcohol group onto propargyl methyl ether complexes. By choosing a different length tether, 7, 8 or 9 membered cyclic ether

alkyne complexes (**18** or **19**) can be produced in good yield (**Figure 9**). The stereoselectivities of the newly formed chiral center are excellent in those processes.

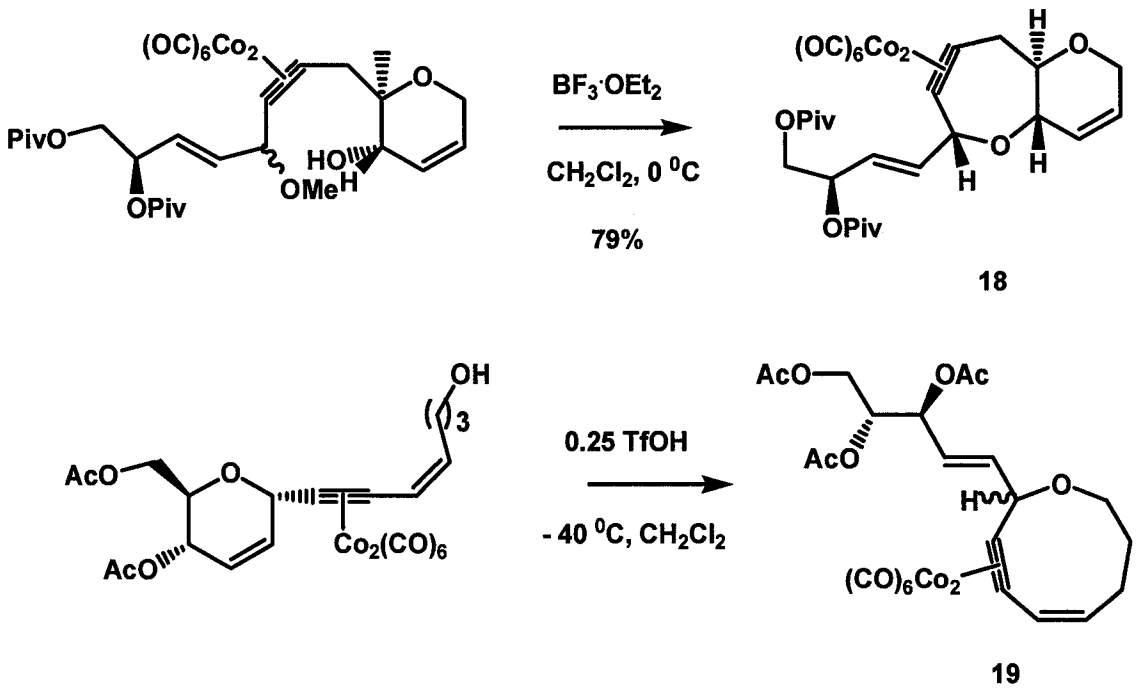


Figure 9 Cycloalkynyl ether formation

Isobe has applied this methodology in natural product synthesis, especially in the work towards ciguatoxin[30] (**Figure 10**). The A ring of this molecule has been synthesized by the reaction in **Figure 9**.

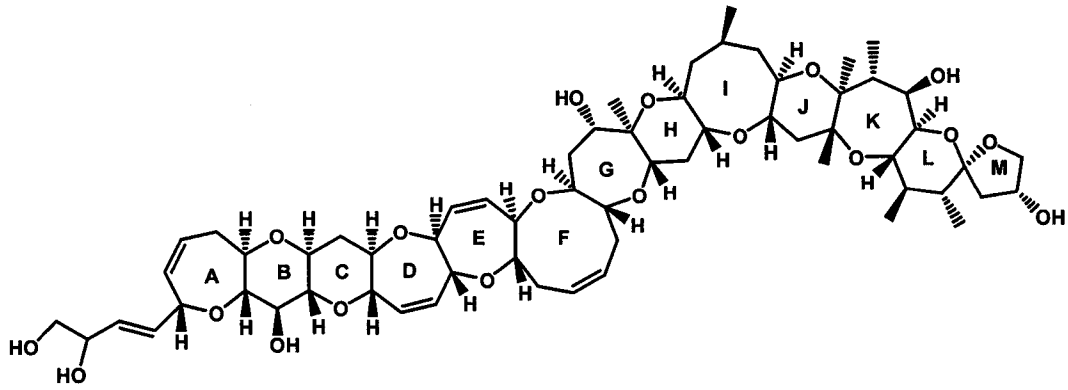


Figure 10 Ciguatoxin (I)

1.4 Macrocycloalkyne Complex Formation

Several groups have produced large ring alkyne complexes by Nicholas chemistry. Isobe's group reported the synthesis of taxane type bicyclo[9.3.1] system **20**, by cyclization of the remote allylsilane unit onto the propargyl cation, in moderate yield.[31] Mays has synthesized sulfur containing macroheterocyclic alkyne complexes **21a** and **21b** (**Figure 11**),[32] by the reaction beween diynediol complex **22,** a dithiol and HBF_4 in excellent total yield.

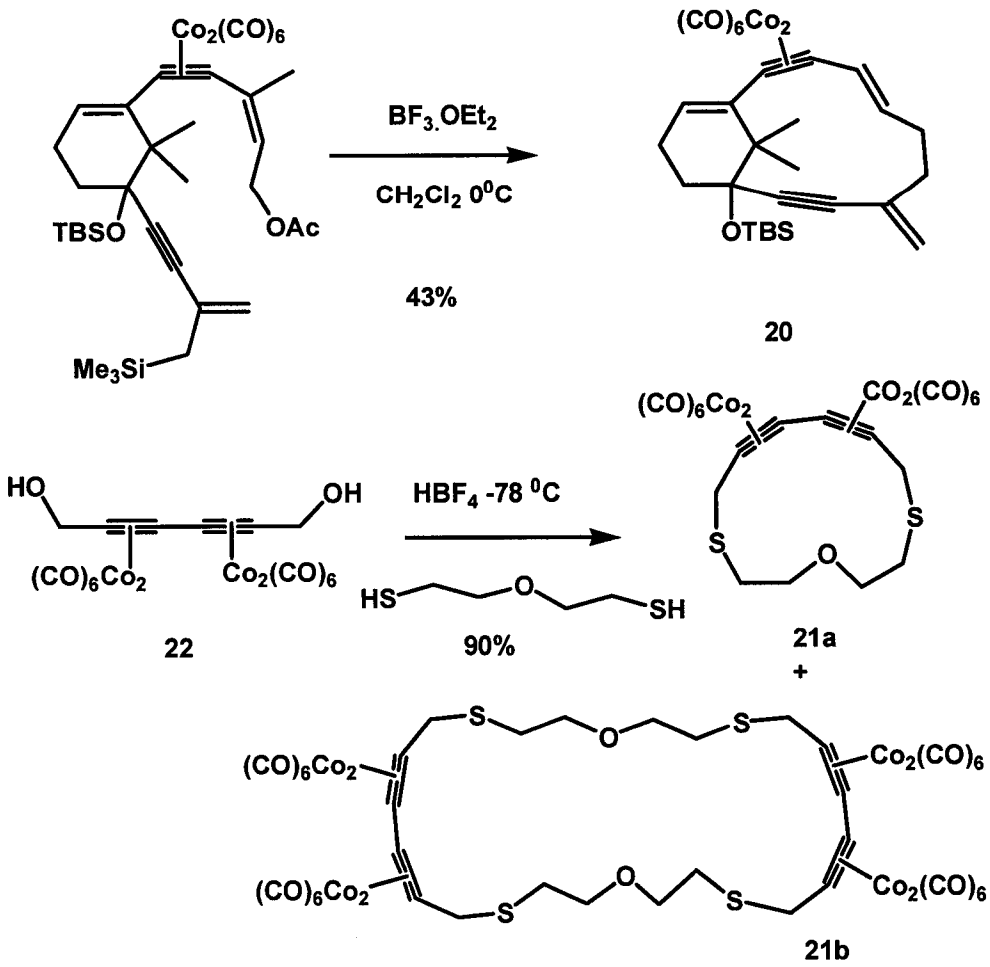


Figure 11 Macrocylic cycloalkynes

Guo and Green have reported the preparation of [7] metacyclophanediyne complexes **23** by reacting diyne complexes with electron rich aromatics. Furan (**24**) and pyrrole (**25**) derivatives were also synthesized analogously (**Figure 12**).[33] The same group has also reported the synthesis of [3.3.3.3] m,p,m,p-cyclophanetetrayne complexes **26** by $BF_3{\cdot}OEt_2$ mediated Nicholas reaction between complex **27** and 1,3,5-trimethoxybenzene.[34]

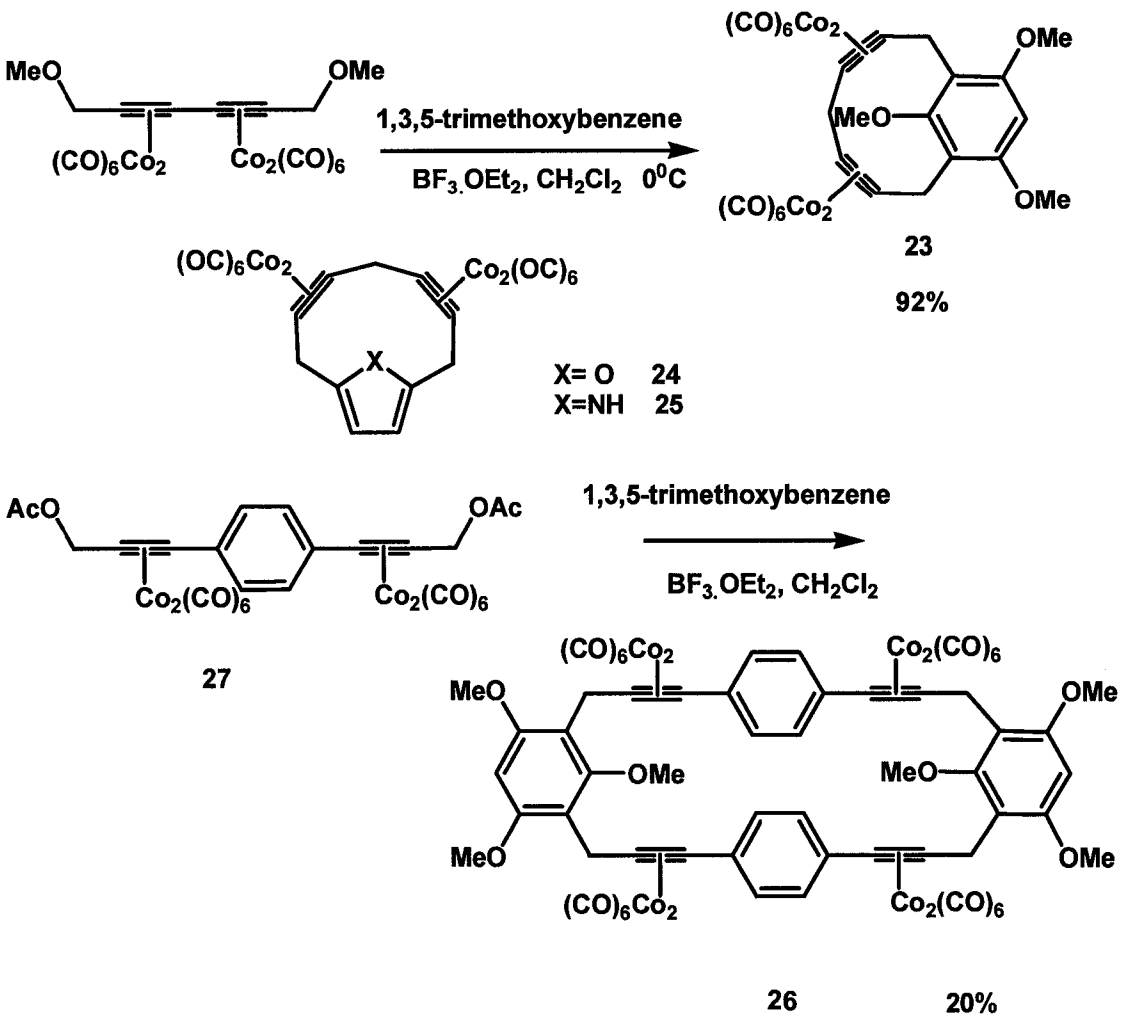


Figure 12 Green group macrocycloalkyne syntheses

1.5 Nicholas reaction with unactived alkenes

Alkenes are sufficiently nucleophilic to be used as effective partners in Nicholas reaction; however, a mixture of regioisomeric alkenes are obtained by competitive H^+ eliminations from the carbocation intermediate (**Figure 13**).[35]

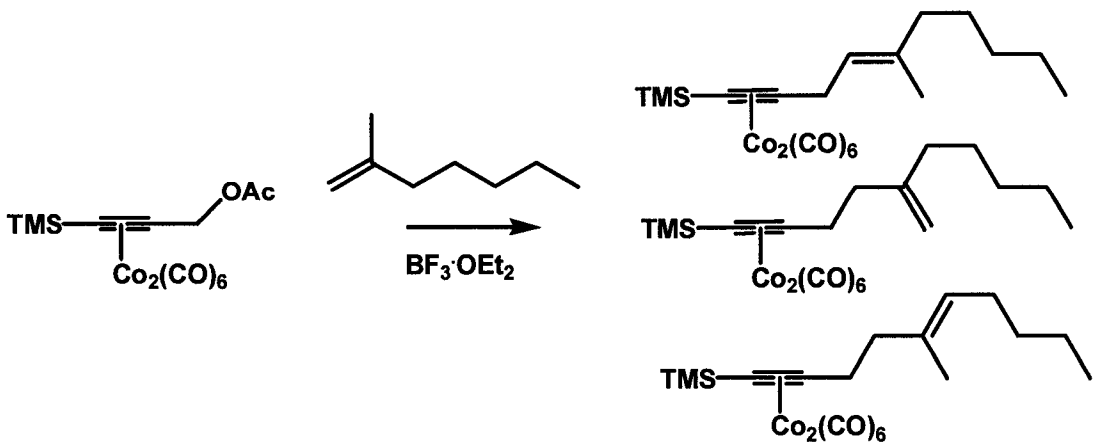


Figure 13 Nicholas reaction of unactivated alkenes

Instead of using an alkene alone, Krafft et al. have employed a terminal alkenyl acid or ester (**28**) in this process. When a remote carbonyl function is present, the carbocation **29** can be trapped intramolecularly by the acid or ester moiety to give lactone derivatives **30** (**Figure 14**).[35]

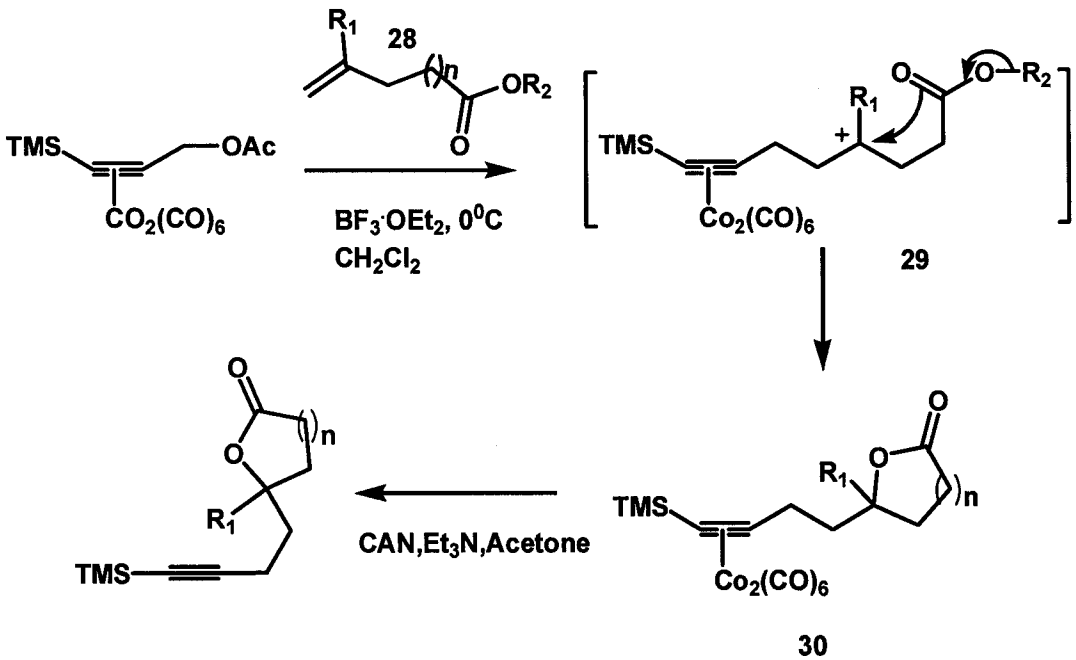


Figure 14 Tandem alkene attack-cation trapping reaction

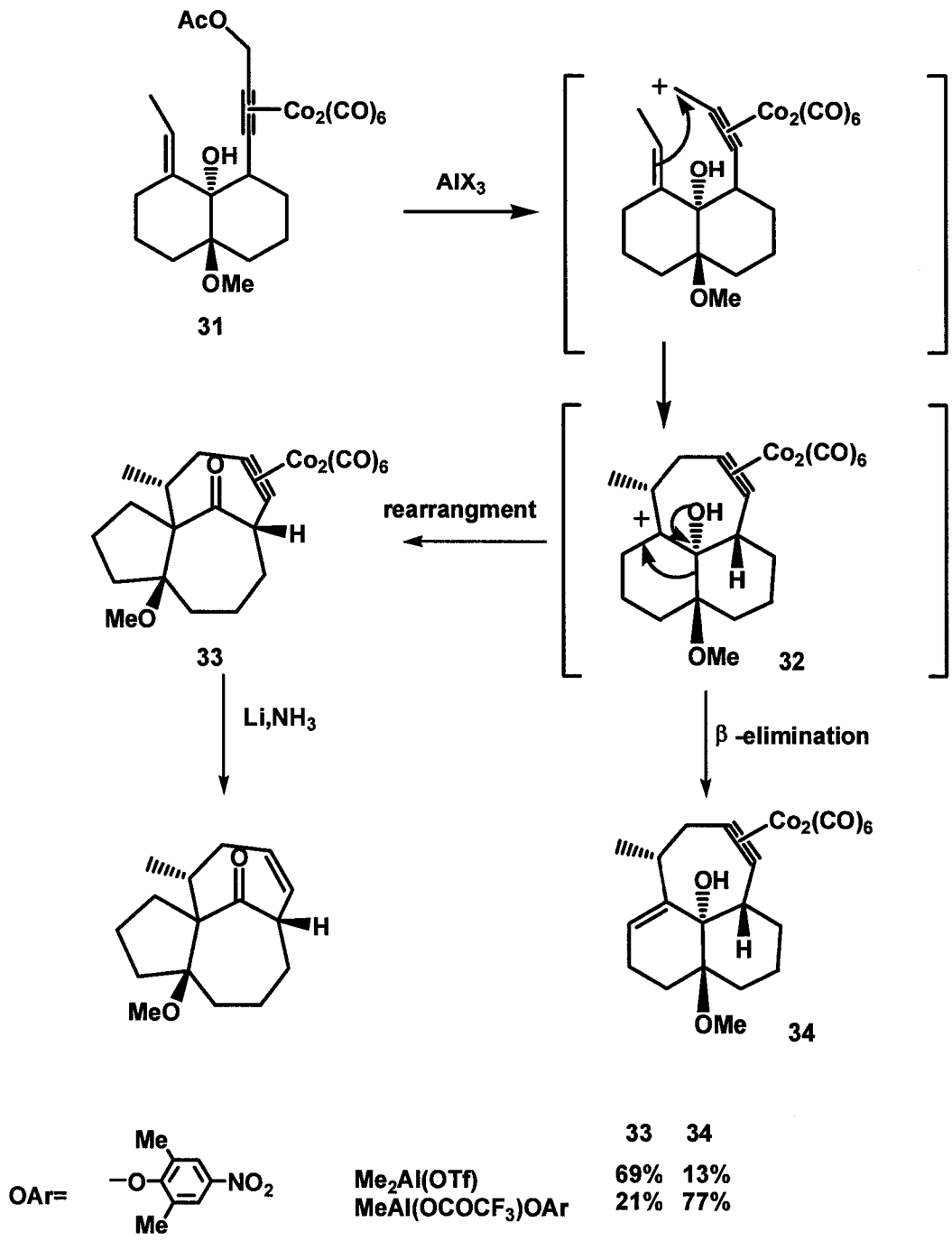


Figure 15 Alkyne trapping-cation rearrangement

Tanino and coworkers have developed a novel approach to a highly strained ingenane skeleton by a tandem Nicholas cyclization – rearrangement (**Figure 15**).[36] Under Lewis acidic conditions, the cobalt complex **31** underwent

intramolecular Nicholas reaction with the available alkene to generate the cationic intermediate **32**, which can neutralize via two pathways. Rearrangement of **32** gives ingenane core **33,** whereas β-elimination gives the complexes **34**. The reaction could be controlled to favor one pathway by choosing the proper Lewis acid.

Tyrrell et al. have shown that a trisubstituted alkene can act as a nucleophile to cyclize upon a benzylic Nicholas type cation, giving benzopyran in a one-pot reaction (**Figure 16**).[37,38] In the reports, treatment of complexed alcohol **35** with HBF_4 generated a tertiary cation (**36**), which was then captured by fluoride ion from HBF_4 to form fluoro compound **37**. Compound **37** was decomplexed by CAN to give the final metal free benzopyran **38** .

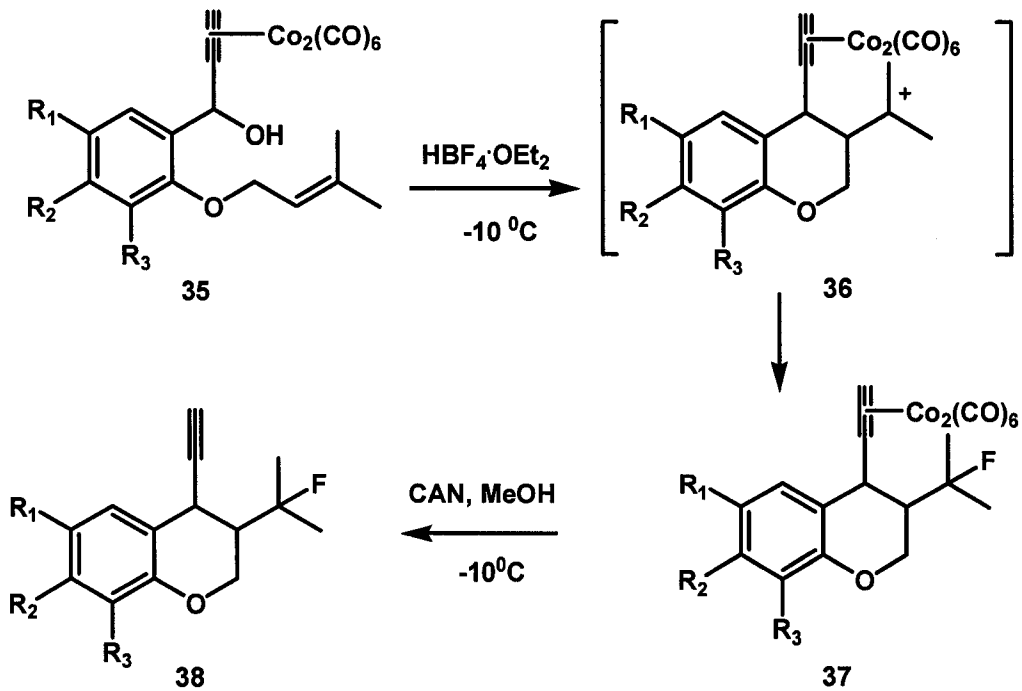


Figure 16 Benzopyran formation and fluoride trapping reaction

When the Green group studied the synthesis of cycloheptyne dicobalt complexes by intramolecular reaction of complex **39**, fluorocycloheptyne complexes **40** were also observed in the process in addition to the major cycloheptyne complex **41** (**Figure 17**).[39,40]

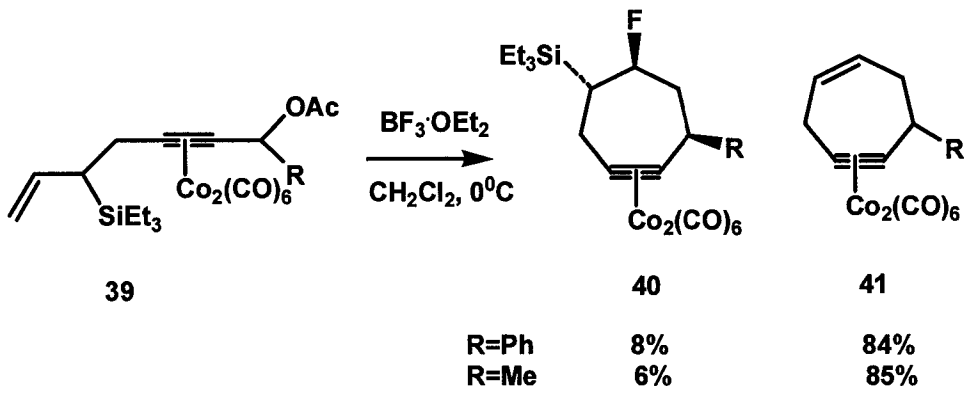


Figure 17 Cyclization to form cycloheptyne complexes

The same group subsequently has extended this process into a one-pot tandem [4+3] cycloaddition/nucleophilic trapping reaction of butyne-1,4-diether dicobalt complexes **42** (**Figure 18**).[41] When allyltrimethylsilane was added to the mixture of complex **42** and $BF_3{\cdot}OEt_2$ (5 equiv), fluorocycloheptyne complexes **43** were produced in good yield. Chloro and bromo cycloheptyne complexes were also obtained when $SnCl_4$ and $SnBr_4$ were in use as Lewis acids, respectively. In order to optimize the reaction conditions for fluorocycloheptynes, the reaction was carried out in a variety of solvents. When the reaction was conducted in benzene solution, Friedel-Craft product **44** was obtained in addition to the flurocycloheptyne (**45**).

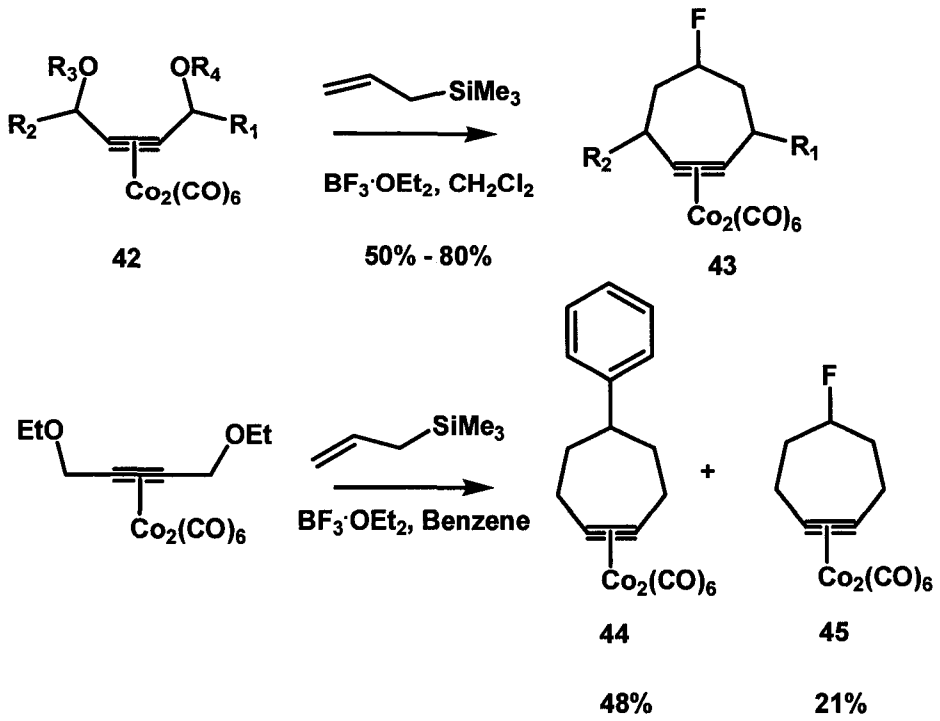


Figure 18 Tandem [4+3] cycloaddition/nucleophilc trapping reactions

The authors have proposed a possible mechanism (**Figure 19**). The reaction between the allyltrimethylsilane and the complex **46** generates the secondary carbon cation intermediate (**47**), which may be trapped by a fluoride source from the conjugate base of the Lewis acid. In benzene solution, benzene apparently traps the cation in the last step. In view of this process, it is reasoned that intramolecular trapping may be possible when a nucleophile is present within the allylsilane (**48**). If this is the case, tricyclic system **50** could be synthesized in a one-pot reaction (**Figure 20**). Attempts to accomplish this type of transformation comprise part of this thesis.

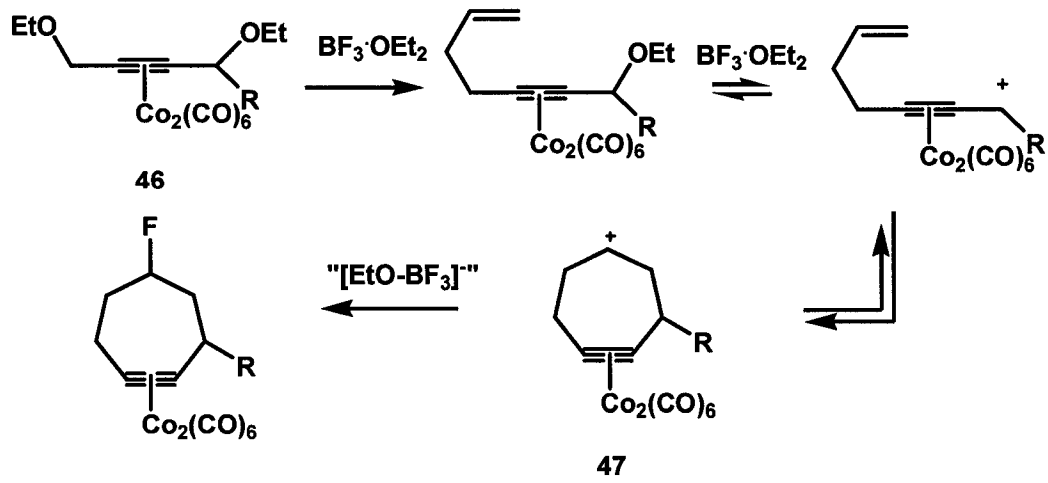


Figure 19 [4+3] Cycloaddition and fluoride trapping reaction mechanism

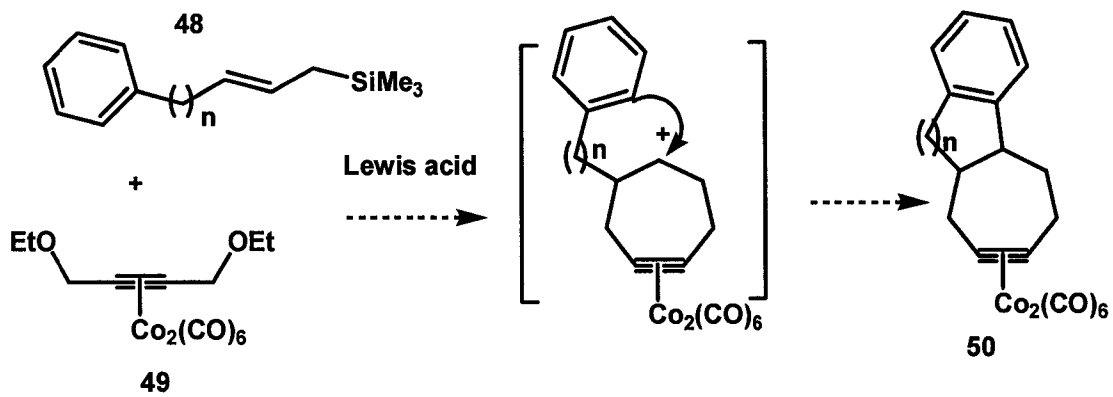


Figure 20 Possible intramolecular trapping

2. Cycloheptyne Dicobalt Complexes Formation by Other Methods

Although the majority of cycloheptyne dicobalt complexes syntheses involve Nicholas reaction chemistry, there exist a limited number of reports of other routes. The Green group has developed an approach to cycloheptyne dicobalt complex formation by ring closing metathesis (**Figure 21**).[42] By using Grubbs (I) catalyst[43], $(Cy_3P)_2Cl_2Ru{=}CHPh$, complexes **51** were easily prepared from the corresponding acyclic diene. Young' s group[44] have studied the medium sized ring (7-9) synthesis by using the metathesis of various similar dienes linked by cobalt hexacarbonyl complexed alkynes by employing Schrock's [45]catalyst.

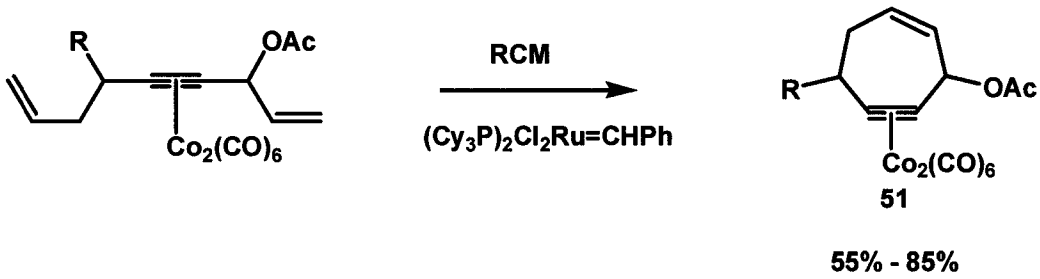


Figure 21 Ring close metathesis of dienyne complexes

Iwasawa and Satoh were the first to report the synthesis of a benzocycloheptyne dicobalt complex, by Heck-type coupling of complexes **52** (**Figure 22**).[46] In order to carry out the palladium catalyzed Heck-type coupling step, two CO ligands of complex **53** were replaced by dppm ligand. The oxidative addition of carbon-iodine bond to palladium (0) gave **54**, which inserted carbon monoxide to give acylpalladium intermediate **55**, and then intramolecular insertion of the olefin to this acylpalladium intermediate **56** followed by β-hydride elimination gave the final 4,5-didehydrotropone-$Co_2(CO)_4$dppm complex **57**. The best CO source was [PhC≡CPh]-$Co_2(CO)_6$.

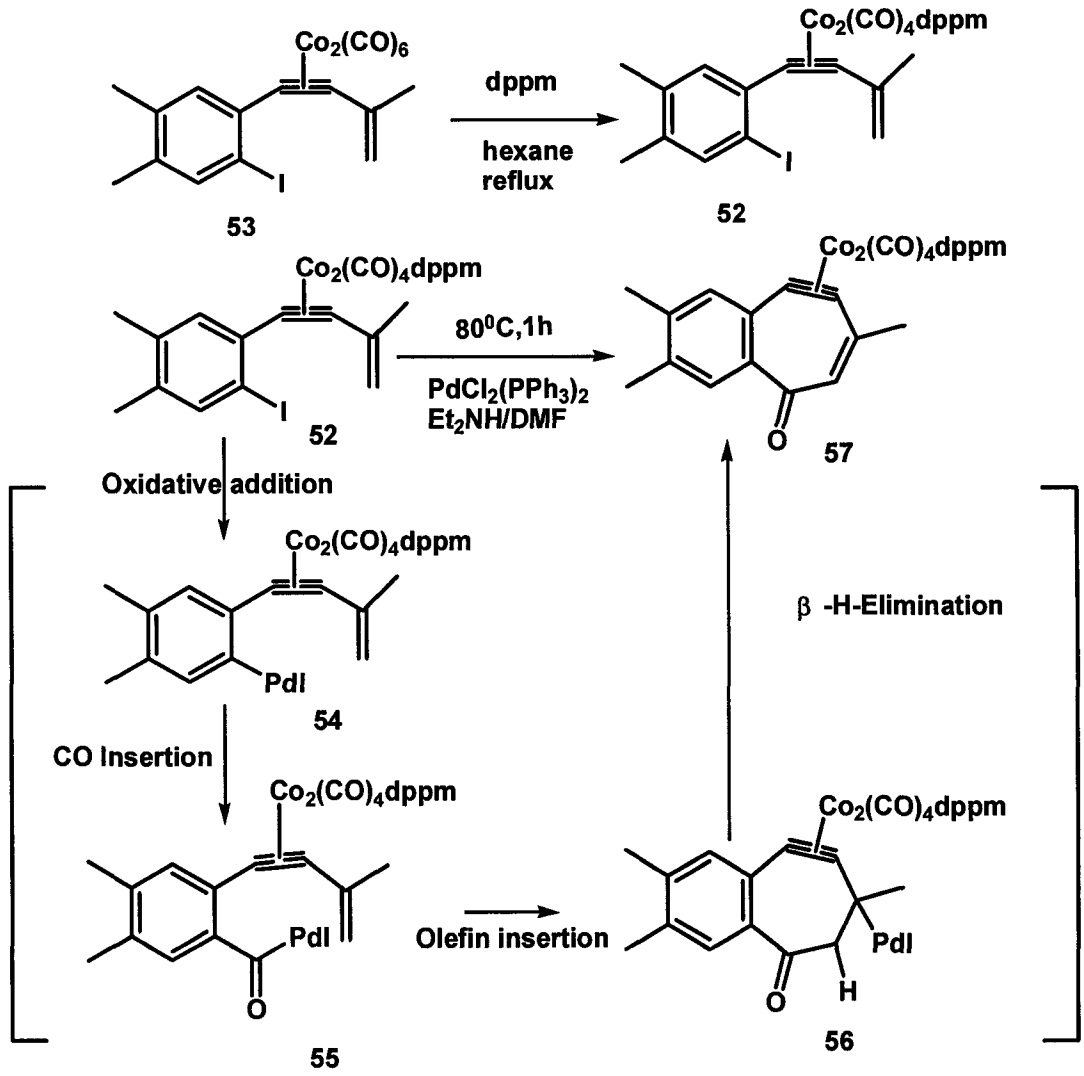
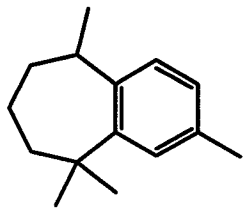


Figure 22 Benzocylcoheptyne complexes formation by Heck-type coupling

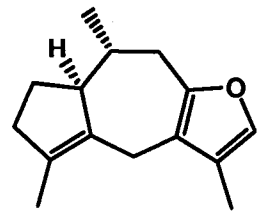
2.1 Benzocycloheptyne Dicobalt Complexes

Benzocycloheptanes containing molecules occur widely in nature (see **Figure 23**), but the methods for rapid synthesis of those ring systems are relatively limited. Despite its inventiveness, the Heck coupling is awkward in its ligand replacement and its necessity for sacrificial cobalt complexes. With the success of several groups' efforts on cycloheptyne dicobalt complex formation,

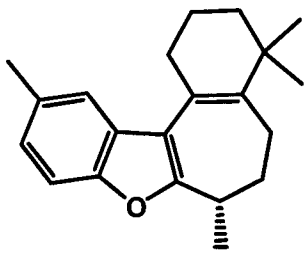
one possible method to synthesize those type compounds is through a dicobalt protected benzocycloheptyne complex pathway.



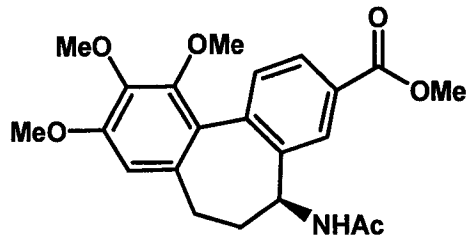
ar-Himachalene



Furanguaian-4-ene



Frondosin B



Allocolchicine

Figure 23 Benzocycloheptane containing molecules

Conversely, with respect to Nicholas reactions, electron rich arenes have been proven to be good nucleophiles. Therefore it is reasonable to believe that it is possible to synthesize benzocycloheptenyne dicobalt complexes **58** by intramolecular Nicholas reactions of arene substituted conjugated (Z) enynyl acetate dicobalt complexes **59**. Compound **59** would be prepared from (Z)-bromoalkene **60** via several steps. The bromoalkene could be synthesized from 2,2-dibromo-1-alkene (**61**), which in turn would be obtained from aldehydes (**Figure 24**).

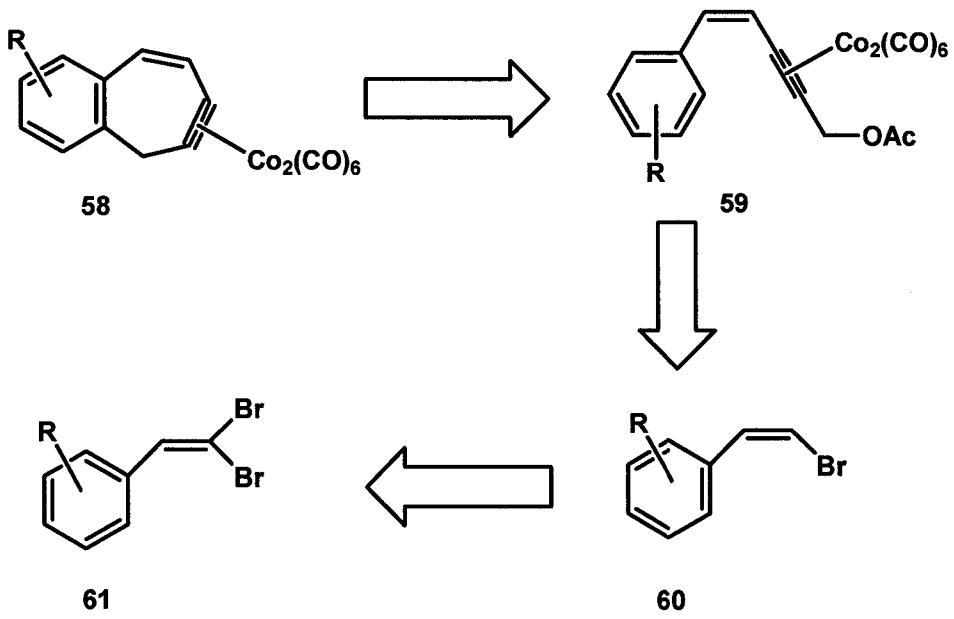


Figure 24 Retro-synthetic route of benzocycloheptenyne complexes

The feasibility of this process, including the scope of the reactions and limitations on the appropriate arenes will be discussed and constitute the major part of this thesis.

3. Cobalt Mediated Cycloadditions

3.1 Pauson-Khand Reaction

A well-known and widely used cobalt mediated cycloaddition is the Pauson-Khand reaction (PKR). It was discovered in 1971,[47] and simply represents a [2+2+1] cycloaddition between an alkyne, an alkene and a CO ligand.

The generally accepted reaction mechanism is shown in **Figure 25**.[48] The first step is a reversible step, involving loss of a CO ligand from one of the cobalt atoms. The alkene coordinates with the unsaturated cobalt in **62** and oxidative coupling of the alkene then creates the first carbon-carbon bond. This is a

regioselective step, in which the alkene inserts into the less sterically hindered site. After CO insertion of **63**, reductive elimination of **64** and decomplexation of cobalt (0) gives the cyclopentenone **65.**

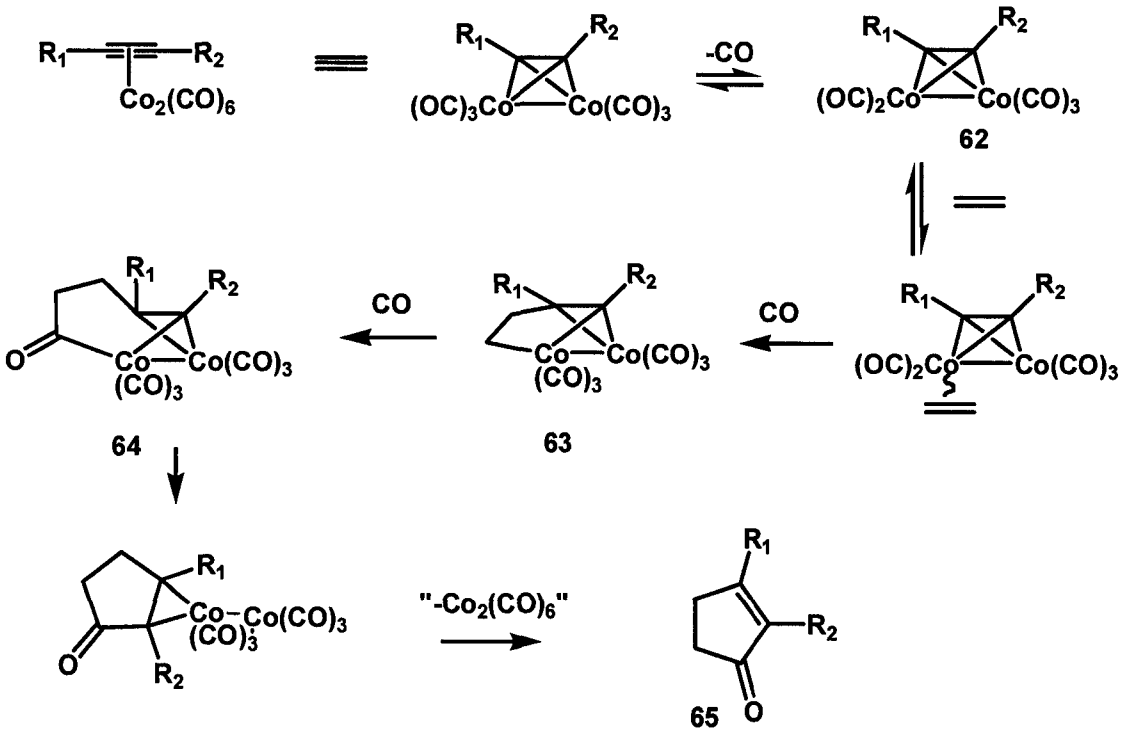


Figure 25 Mechanism of Pauson-Khand reaction

Both intermolecular and intramolecular Pauson-Khand reactions have been reported. In intermolecular Pauson-Khand reactions, unstrained alkenes are known to be much less reactive than strained ones and give lower yields of cyclopentenones. In addition, regioisomers are obtained when unsymmetrical alkenes are reacted with terminal alkynes (**Figure 26**).[49]

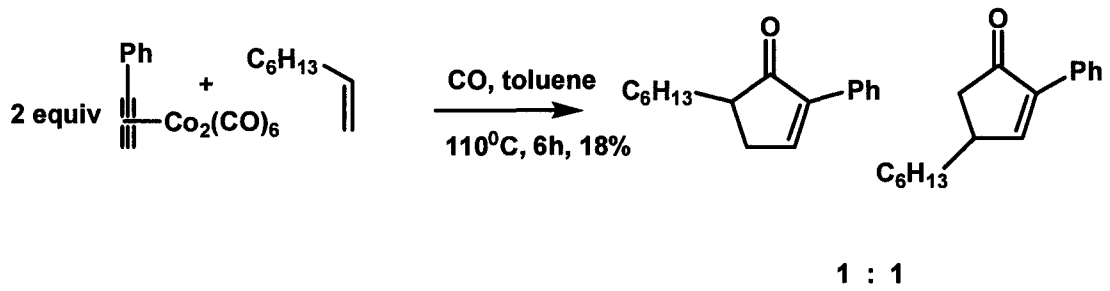


Figure 26 Intermolecular Pauson-Khand reaction

Due to the regioselectivity and yield limitations, most recent researchers have focused on intramolecular Pauson-Khand reactions, which constitute a method for the rapid synthesis of bicyclic pentenone derivatives. A simple example is demonstrated below (**66**, **Figure 27**).[50]

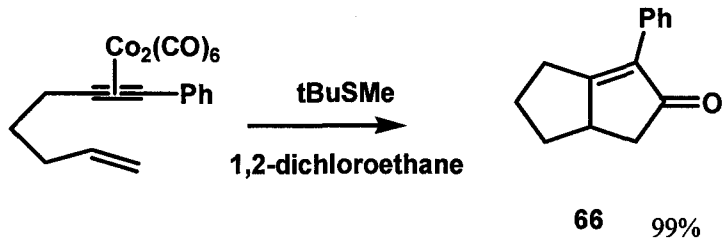


Figure 27 Intramolecular Pauson-Khand reaction

3.2 Cobalt mediated [2+2+2] cycloadditions

Alkyne functions groups often have been converted to six membered ring systems by [2+2+2] cycloadditions.[51] For metal free alkynes, several transition metals have been successfully applied in the reaction, including Pd (0), Rh (I), and Ni (0), most of which were employed as catalysts.[52] However, cobalt (I)

centered reagents such as $CpCoL_2$ (L=CO, ethane) have also been used most extensively in this type reaction (**Figure 28**).[53]

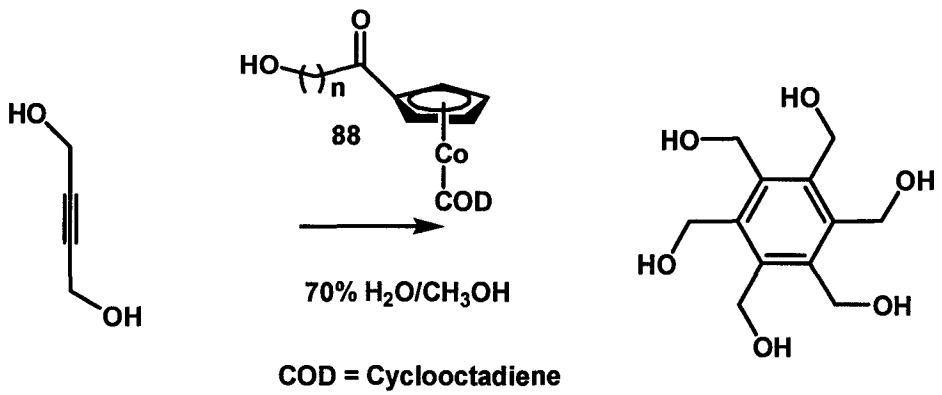


Figure 28 Cobalt (I) mediate [2+2+2] cycloaddition

Green's group first reported a cobalt (0) mediated [2+2+2] cycloaddition on cycloheptyne dicobalt complexes (**Figure 29**).[54] When the diyne ether complex **67** was exposed to a series of alkynes under reflux in toluene, fused [7,6,5] systems (**68**) were synthesized in ca. 60% yield. In the same publication, they reported an all-intramolecular [2+2+2] cycloaddition of compound **69**; the final products **70** retained the stereochemistry present in **69**

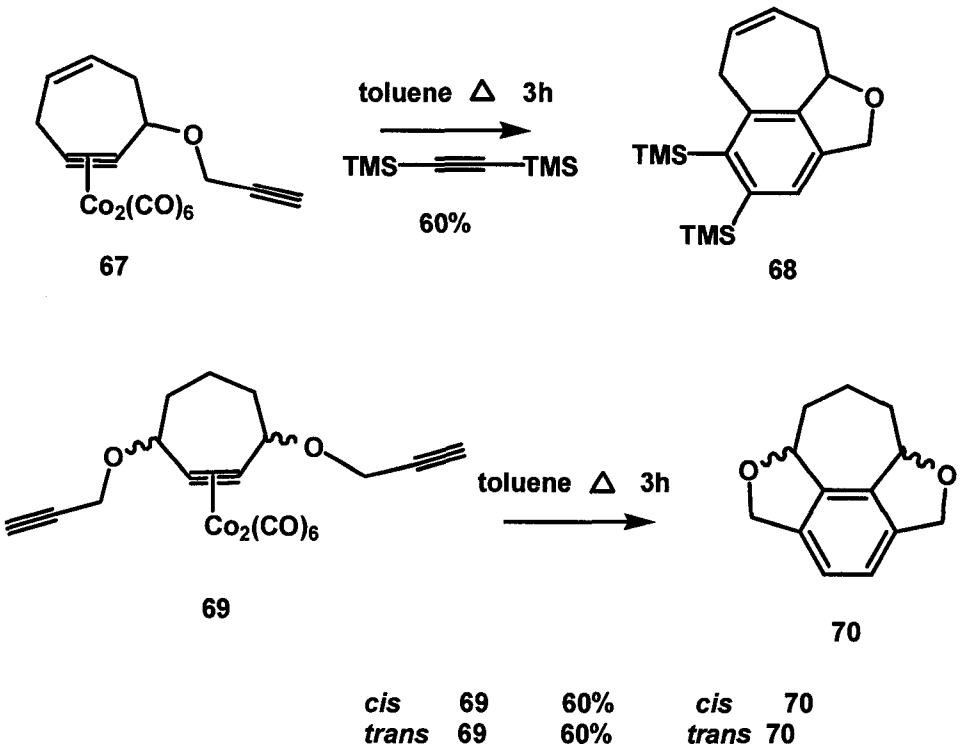


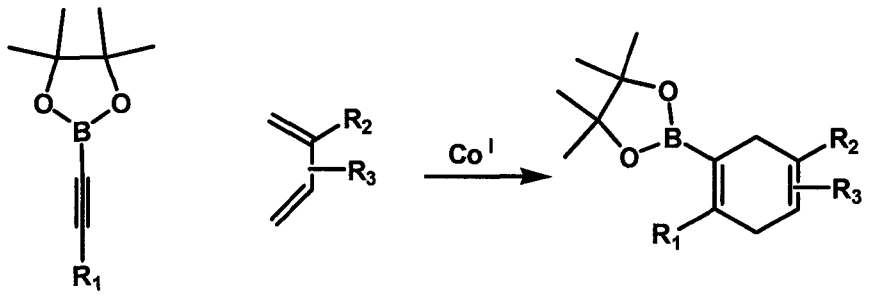
Figure 29 [2+2+2] Cycloaddition of cycloheptyne dicobalt complex

3.3 Cobalt Mediated [4+2] Cycloadditions

The Diels-Alder reaction has been known for many decades.[55] It provides a rapid route to form a six-membered ring from an electron-deficient alkene or alkyne and a diene. Numerous natural products have been synthesized from intermolecular or intramolecular versions of the Diels-Alder reaction.[56] However, to carry out a Diels-Alder reaction of an unactivited alkyne, high temperatures or catalysts are often required in the process. Titanium[57], iron[58], ruthium[59] and nickel[60] based catalyst are commonly used. Recently, cobalt catalysts have been investigated in the reaction.

Hilt and Smolko have reported the cobalt (I) catalyzed cycloaddition of alkynylboron compound **71** with acyclic 1,3-dienes under mild conditions to

generate the corresponding dihydroaromatic vinylboron compounds **72** in good yield (**Figure 30**).[61]



71 72

Figure 30 Cobalt(I) mediated intermolecular Diels-Alder reaction

Lautens et al. have described the intramolecular [4+2] cycloaddition between norbornadiene and an unactivated acetylene by using $Co(acac)_2$ as catalyst , which has been reduced to Co (I) by Et_2AlCl in the process (**Figure 31**).[62]

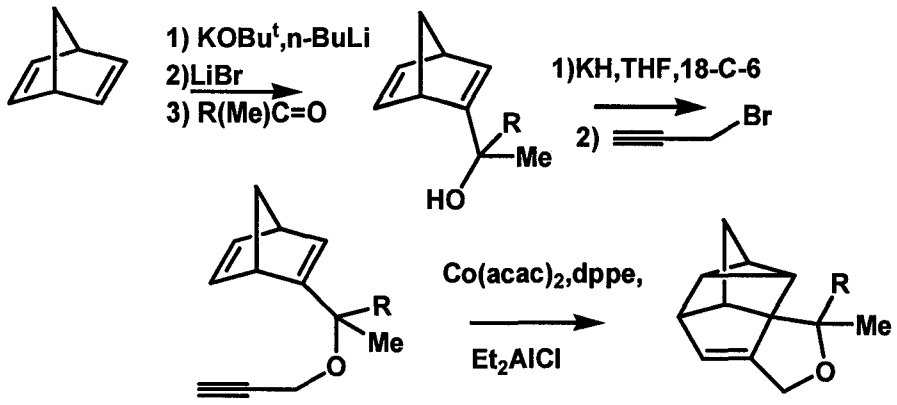


Figure 31 Cobalt(I) mediated intramolecular [4+2] cycloaddition reaction

Metal complexes of unstable systems have been employed as precursors in Diels-Alder reactions. Snapper and coworkers reported the first intramolecular cycloadditions between cyclobutadiene iron complexes and unactivated olefins to produce novel cyclobutene containing systems (**Figure 32**).[63] The iron complexed cyclobutadienes **73** were decomplexed by oxidative reagent CAN to give metal free butadiene **74**, which is highly strained, unstable and highly reactive. In the presence of a tethered alkyne, cycloaddition occurs, followed by isomerization to arene **75** induced by thermolysis.

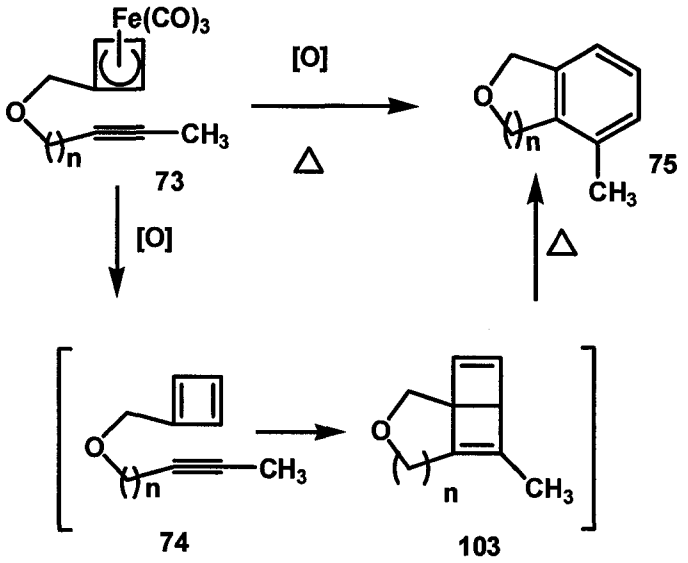
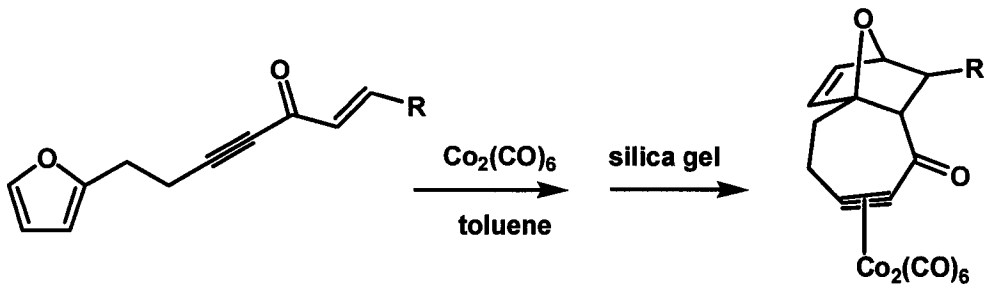


Figure 32 Diels-Alder reaction of iron complexed butadiene

Iwasawa et al have applied the change of structure of alkyne in cobalt complexes to a complex-initiated Diels-Alder reaction (**Figure 33**).[64] On absorbing onto silica gel, the alkyne-$Co_2(CO)_6$ complexes **76**, bearing a diene and a dienophile at the opposite ends of the alkyne, a Diels-Alder reaction

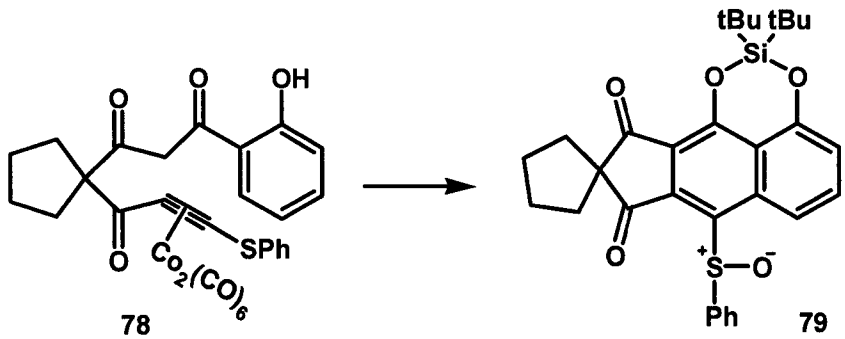
occurred to give the adduct **77**. The equilibrium for seven-membered ring product formation on silica gel was greater than that in solution.



76 **77**

Figure 33 Cobalt initiated Diels-Alder reaction

Kita et al have synthesized fredericamycin A from cobalt complexes by employing an oxidative intramolecular Diels-Alder reaction (**Figure 34**).[65] When chloroanil was added to **78**, the cobalt moiety was oxidized from the triple bond, which in turn underwent [4+2] cycloaddition and oxidation at the sulfur atom gave the final product **79** in good yield.

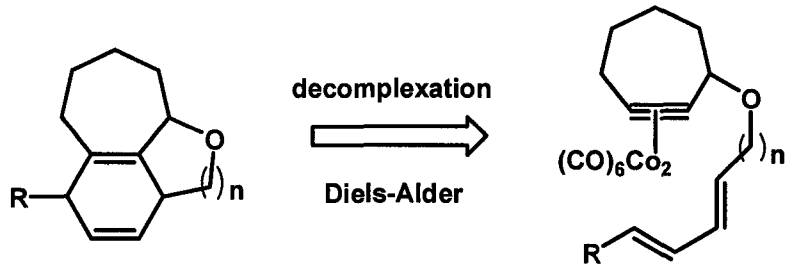


78 **79**

1.Me_2SiCl_2, Et_3N, chloranil, 100 ^0C, 2. $tBu_2Si(OTf)_2$, Et_3N, 3. mCPBA

Figure 34 Diels-Alder reaction of cobalt (0) complexes

Theoretically and experimentally, the angle strain of cycloalkyne makes the triple bond of metal free cycloheptynes very reactive and unstable. By analogy to use of cyclobutadiene-iron complexes by Snapper, it would appear likely that under proper conditions, the triple bond of cycloheptyne complexes **80** could be made to react with dienophiles to undergo [4+2] cycloadditions by smoothly releasing the dicobalt-protecting group. The attempts to bring this concept into practice form a part of the thesis. (**Figure 35**)



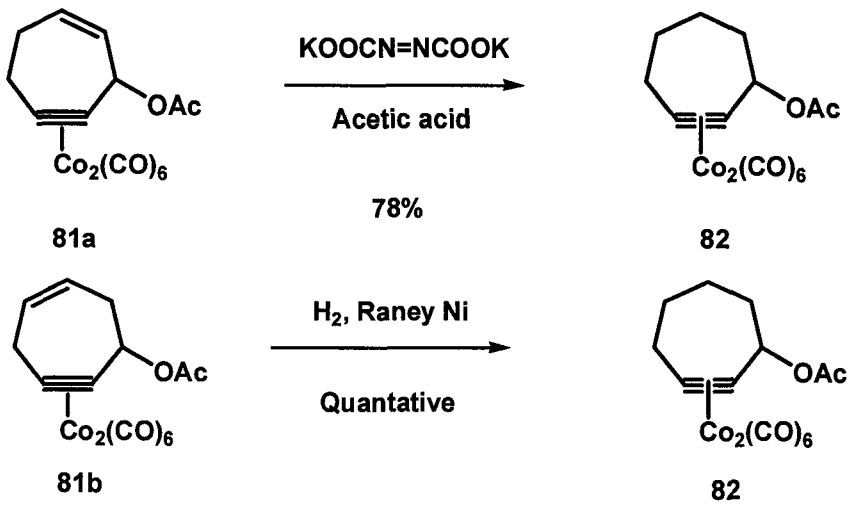
80

Figure 35 Possible [4+2] intramolecular Diels-Alder reaction

Results and Discussion

1. Intramolecular Diels-Alder Reactions of Cycloheptyne Complexes.

Green and his coworkers have thoroughly studied the formation of cycloheptenyne dicobalt complexes **51** by ring closing metathesis.[42] To perform intramolecular Diels-Alder reactions of cycloheptyne complexes **80**, the cycloheptenyne complexes **81a** must be reduced at the double bond to afford cycloheptyne complex **82** without affecting the dicobalt protecting group and the triple bond. Raney nickel conditions, which quantitatively reduce compound **81b** to the corresponding cycloheptyne complex **82**,[54] do not work in this particular case. This step was accomplished on **81** by using diimide (HN=NH), via the potassium azodicarbonate[66] (KOOCN=NCOOK) as reducing reagent precursor, to give desired product **82** in 78% yield (**Scheme 1**). An excess amount of KOOCN=NCOOK was needed in the process (5 equiv).



Scheme 1 Reduction of cycloheptenyne complex

In order to enable the [4+2] intramolecular cycloaddition, a conjugated diene functional group was appended to the cycloheptyne complex system. We chose those groups that appeared suitable for introduction by Nicholas reaction chemistry, using Lewis acid mediated reactions of compound **82** with acids or alcohols containing a diene function. Generally, the cycloheptyne complexes **82** were reacted with excess dienophile (10 equiv) in the presence of $BF_3.OEt_2$ (5 equiv) at 0^0C. The results are shown in **Table 1**.

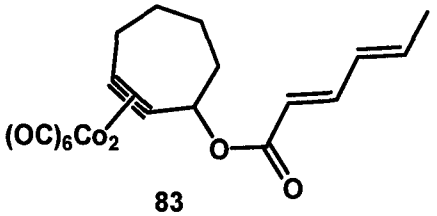
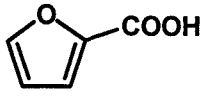
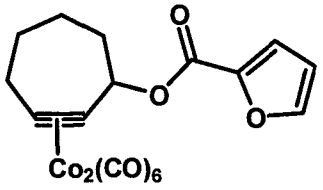
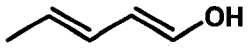
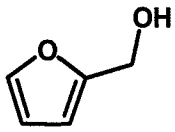
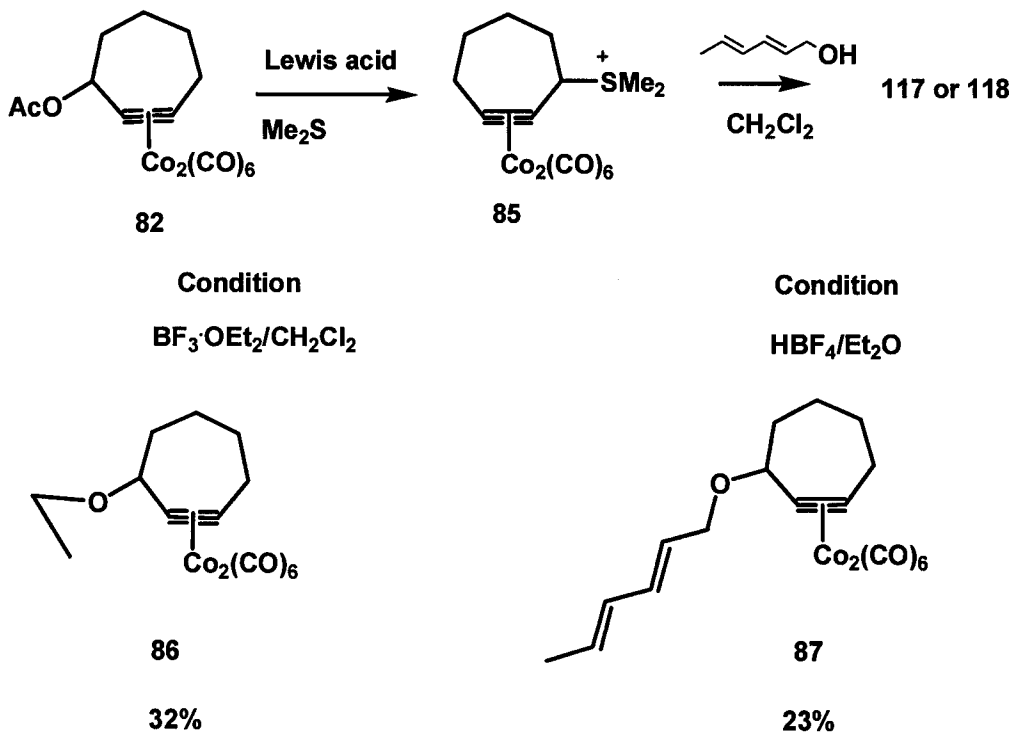
Dienophile	Product	Yield
	 **83**	**70%**
	 **84**	**77%**
	**polymer**	
	**no reaction**	

Table 1 Result of Nicholas reaction with dienophiles

As can be seen from **Table 1**, sorbic acid and furoic acid participated in Nicholas reactions very well and gave the condensation products in good yield, specifically 70% for compound **83** and 77% for compound **84**. Unfortunately the corresponding Nicholas reaction products expected from *trans,trans* 1,4–hexadien-1-ol and 2-furfuryl alcohol could not be achieved under the same conditions. With *trans,trans* 1,4–hexadien-1-ol, a highly viscous material resulted, likely due to polymerization of diene in the presence of the Lewis acid. An attempt was made to obtain the dienyl ether by way of the propargylsulfonium salt **85** of the cobalt complex.[67] The Lewis acid was added to compound **82** and Me_2S (10 equiv.) in the appropriate solvent solution (see **Scheme 2**); after 1 hour, all the volatile materials were removed, the residue was dissolved in CH_2Cl_2 and the dienol was then added into the solution (**Scheme 2**). Surprisingly, when $BF_3{\cdot}OEt_2$ was used in CH_2Cl_2 solution, instead of the intended product, compound **86** was formed. The possible reason for this phenomenon is the Et_2O ligand of the Lewis acid attacking the sulfonium salt, with F^- ultimately removing an ethyl group. Fortunately, when the Lewis acid $BF_3{\cdot}OEt_2$ was replaced by HBF_4 and diethyl ether was used as solvent, the desired product **87** could be synthesized, although in poor yield (23%). This substitution was slow, and the rest of cobalt complex had been decomposed (**Scheme 2**).

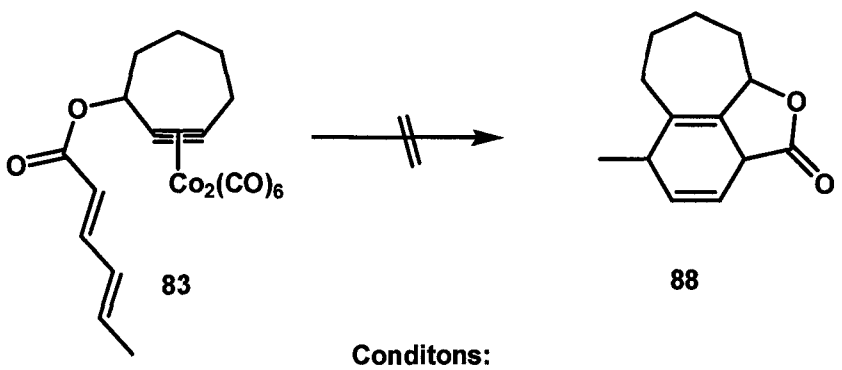


Scheme 2 The formation of cycloheptyne dienyl ether

As for the 2-furfuryl alcohol substitution, the Nicholas reaction never occurred regardless of the amount of Lewis acid added. Only a small amount of furfuryl alcohol was recovered; most of it may be decomposed by the Lewis acid.

With the dienyne complexes readily in hand in two cases, the Diels-Alder reactions were carried out by Snapper's [63] (CAN oxidant) and Kita's [65] (chloranil oxidant) methods. Unfortunately, no isolable products were obtained after removing the dicobalt moiety by oxidizing reagents. (**Scheme 3**) Several oxidizing reagents known to remove dicobalt units were applied in this process, including CAN, chloranil, and trimethyl amine N-oxide. Under Kita's condition, only a trace of potential product was seen by ^{1}H NMR spectroscopy, but it

couldn't be purified. When CAN or Me_3NO was used, no product was evident by ^1H NMR spectrospcopy. Those reagents are strong oxidants, while the metal free cycloheptyne is highly reactive species. As a result, it is quite likely that the cycloheptyne was destroyed by the oxidants prior to undergoing [4+2] cycloaddition.

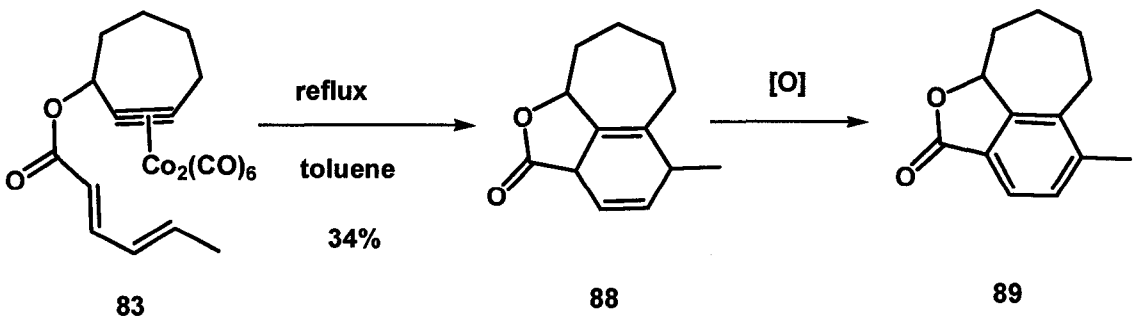


83 **88**

Conditons:
1.Chloroanil (4 equiv) benzene (1mM) 90 ^{0}C
2 CAN (4 equiv) acetone (1mM) RT
3 $Me_3NO.\ 2H_2O$ (4 equiv) acetone (1mM) RT

Scheme 3 Diels-Alder reaction with oxidizing reagents

Limited success was possible by omitting the oxidant entirely. By simply refluxing the dienyne **83** in toluene for 3 hours, a fused [7,6,5] ring system **88** was obtained in 34% yield as a white solid. The cyclohexadiene unit slowly oxidized to an aromatic ring (**89**) in the air (**Scheme 4**). We were encouraged by this modest success, but the yield could not be improved by controlling the reaction time.

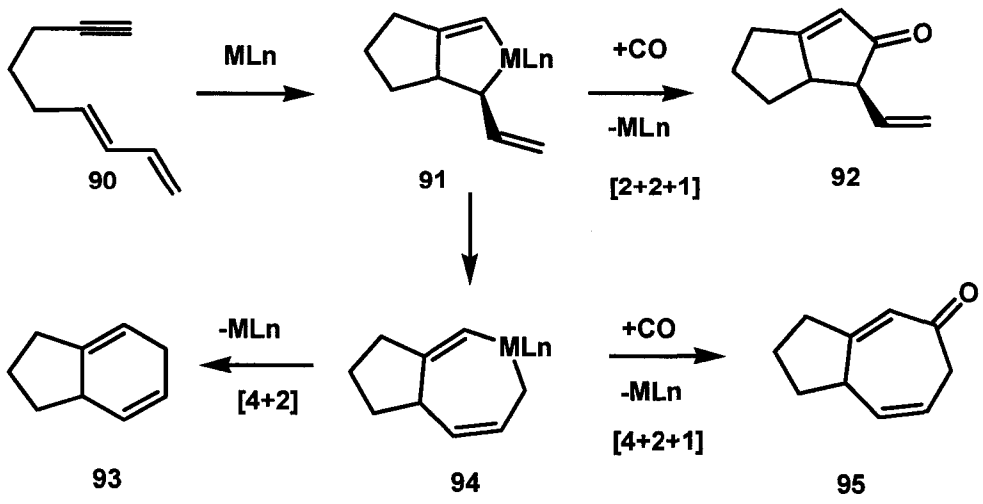


83 88 89

Scheme 4 [4+2] Cycloaddition of dienyne

The **83→89** transformation is a special case of an inverse electron demand Diels-Alder (IEDDA) reaction. Normally, electron deficient dienophiles and the low reactivity of an unactivated alkyne as a dienophilic reagent have proven to be a major limitation of the Diels-Alder reaction. In most acyclic cases, extremely high temperatures or catalysts are required.[68] Here, the reaction was carried out under relatively mild conditions and without any catalyst mediating the process. A possible reason for this is that the cobalt was involved in the reaction.

The mechanistic end of this process is not clear. The reaction pathway may be similar to the mechanism proposed by Wender[69] (**Scheme 5**). Three competing metal-catalyzed cycloaddition pathways are available for a dienyne in the presence of CO: an intramolecular [4+2] cycloaddition (**90→93**), an intramolecular Pauson-Khand [2+2+1] cycloaddtion (**90→92**) and a [4+2+1] cycloaddition (**90→95**). In the desired reaction, the cobalt coordinates with the double bonds and undergoes oxidative coupling to give the intermediate **91**. Since there was a limited amount of CO present, the reaction is favored to proceed through a reductive elimination pathway to give the [4+2] product.



Scheme 5 **Possible competing cycloaddition pathways**

Unexpectedly, there was no product shown in the ^{1}H NMR spectrum under the same conditions as **83** for compound **84**. The attempts to accomplish an analogous [4+2] cycloaddition on furoic ester **84** or dienyl ether **87** under oxidative or thermal conditions gave no tractable reaction products. In view of the limitation and lack of generality of this cycloaddition process, further attempts at the Diels-Alder reaction of these cycloheptynes were not pursued.

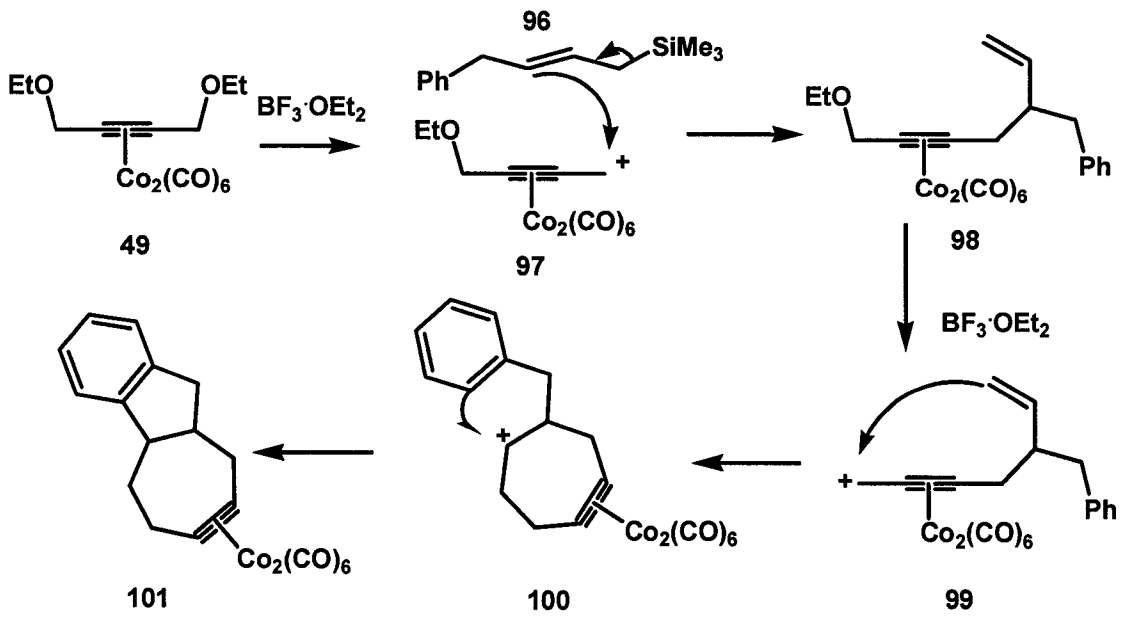
Conclusion

It has been found that the sorbic acid and 2-furoic acid were good nucleophiles for Nicholas reaction of cycloheptyne propargyl acetate complex **2** under normal conditions. Compound **87** was obtained by a propargyl sulfonium salt pathway in poor yield. No expected product was achieved for 2-furfuryl alcohol due to decompostion of the alcohol in the presence of Lewis acid.

The possibility of an intramolecular [4+2] cycloaddition of cycloheptyne dicobalt hexacarbonyl complexes has been shown. Only one particular case (**89**) has been carried out successfully, in 34% yield.

2. [4+3] Cycloaddition/intramolecular Trapping Reactions of Propargylic Diether Dicobalt Complexes via Sequential Nicholas Reactions.

Green and Lu have studied in depth the [4+3] cycloaddition of allylsilane with propargylic diether dicobalt complexes in tandem with nucleophilic trapping the resultant cationic intermediates.[41] We reasoned that by incorporating a nucleophile in a judicious manner within the allylsilane, the final nucleophilic trapping process could be made intramolecular, and bicyclic or tricyclic systems could be assembled in one synthetic operation. To investigate this process, trimethyl(4-phenylbut-2-enyl)silane (**96**) was employed in a Lewis acid mediated reaction with **49**. The entire process and mechanism is shown in **Scheme 6**, ideally giving polycyclic system **101** in one-pot. Compound **96** was prepared from benzoyl chloride, hexamethyldisilane and butadiene by the aid of $Pd(dba)_2$ [70] as catalyst. [71]

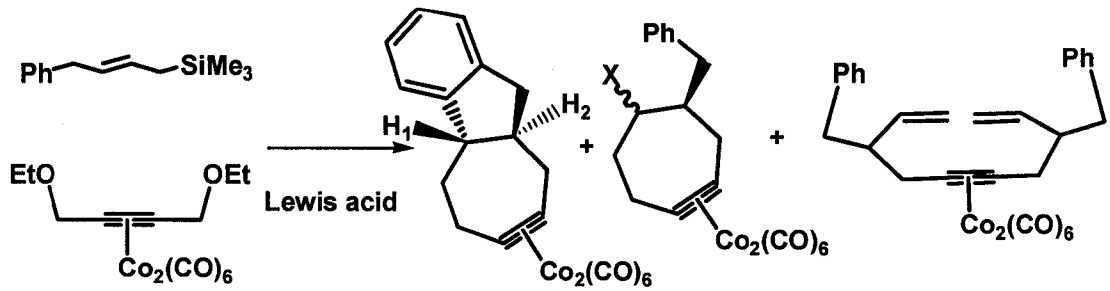


Scheme 6 [4+3] Cycloaddition and intramolecular trapping reaction mechanism

The reaction between allylsilane (**96**) and the $Co_2(CO)_6$ stabilized propargyl cation **97** would form **98**, which would in turn ionize in the presence of $BF_3{\cdot}OEt_2$ to give propargyl cation **99**. The cyclization of **99** would then give 2° alkyl cation **100,** which we anticipated would be intramolecularly trapped by the arene ring, eventually obtaining Friedel-Crafts alkylation product **101**.

When reactions were performed under similar conditions to those published,[41] the intended **101** could be isolated, but several other products were also obtained. Besides the intended product, the major side products were halogenation complexes (**102,103**), which have been seen in Lu's work even when benzene was used as solvent. It could be contented that in the last trapping step, the halogen ions from the Lewis acid are better nucleophiles than arenes, and they are also probably present as tight ion pairs, so that

halogenations were effectively competing reactions with the Friedel-Craft alkylation. In addition, diallyation complex **104** was also formed in the process.



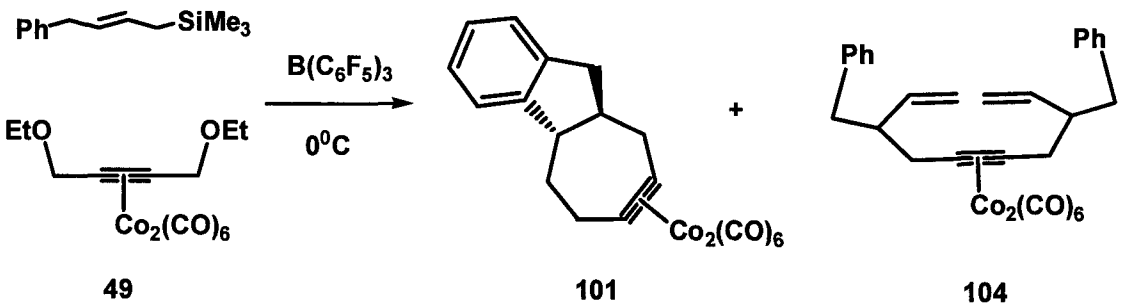
Lewis acid				
	$BF_3 \cdot OEt_2$	X=F	102	104
	$SnCl_4$	X=Cl	103	104

Scheme 7 [4+3] Cycloaddition trapping results with halide Lewis acids

Various Lewis acids were investigated in the process. When $BF_3 \cdot OEt_2$ was used as Lewis acid, compound **101** was formed in 20% yield, while the fluorination product **102** and diallylation complexes **104** could be isolated in 54% and 18% yield. If $SnCl_4$ was used, **101**, **103** and **104** were obtained in 14%, 38% and 14% respectively. The product **101** obtained in both cases was to be *trans* isomer exclusively as evident by the ^1H NMR spectroscopy resonance for the benzylic methine (H_1: δ 2.88,apparent t, J=10 Hz) indicating two trans diaxial coupling constant. The ratios of stereoisomers of the two halogenation products were near 1:1(*cis: trans*).

$SnBr_4$ was also used in the reaction, but no compound **101** or bromination complexes were formed, and only a small amount of diallyl product was seen. The majority of the starting complex **49** had been decomposed.

In order to eliminate the halogenation side reactions, several Lewis acids were investigated including those with and without a halide source. Me_2AlCl, Bu_2BOTf, $Me_2Al(OCOCF_3)$ were applied in the reaction. Unfortunately no promising results were obtained. When dimethylaluminum chloride was used, no reaction occurred at all, while the other two Lewis acids caused extensive decomposition.

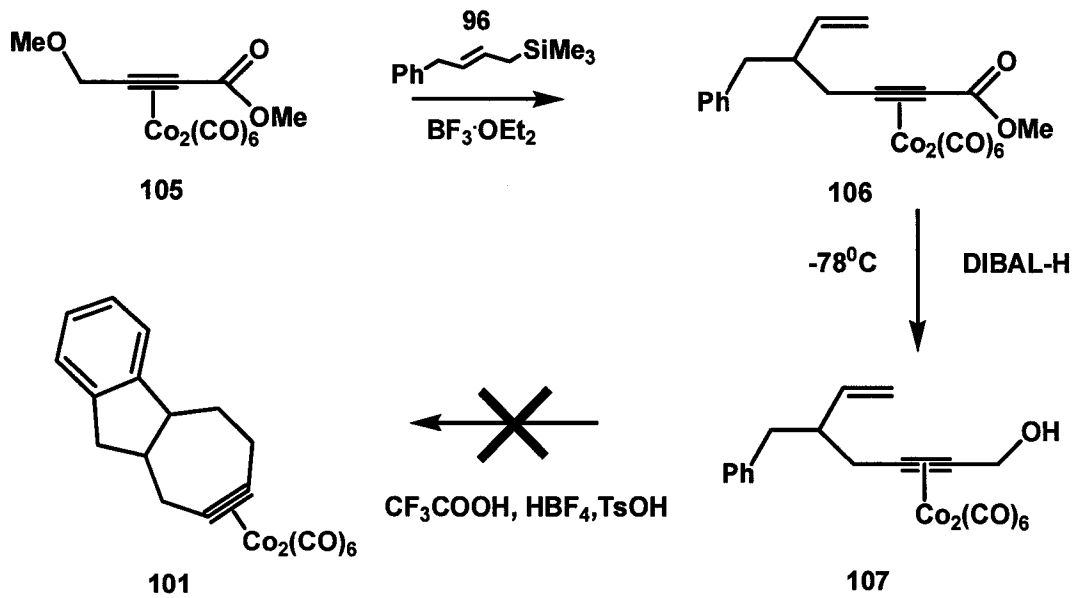


49 **101** **104**

Scheme 8 $B(C_6F_5)_3$ mediated reaction result

$B(C_6F_5)_3$ was finally found to be the best Lewis acid for formation of the trapping product **101**. When 3.5 equiv of $B(C_6F_5)_3$ in CH_2Cl_2 was added slowly to the mixture of compound **49** and allylsilane **96** at 0^0C, product **101** was obtained in 38% yield, while diallyl complex **104** was formed in 20% yield; no halogenation complexes were formed since no halide ion was present in the reaction mixture.

The addition mode and reaction temperature were critical in this process. When the allylsilane **96** was added to the mixture of **49** and the Lewis acid at room temperature, all the starting materials were decomposed. Upon slow addition of the Lewis acid to the mixture of compound **49** and nucleophile **96**, only 23% of product **101** were obtained when the reaction was carried out at room temperature. When the reaction was attempted at -30^0C, no reaction occurred at all.



Scheme 9 Stepwise synthetic route

To avoid the diallyl side product, a stepwise synthesis was investigated that incorporated with allylsilane in a separate step (**Scheme 9**). Instead of using a propargylic diether dicobalt complex, γ-methoxy ester **105** was used as the starting material. By using $BF_3{\cdot}OEt_2$ as the Lewis acid and allylsilane **96** as nucleophile, compound **106** could be obtained in 60% yield (80% based on recovered starting material); complex **106** in turn was reduced to alcohol **107** by

DIBAL-H at -78^0C. Unfortunately, the cyclization step could not be completed by treating the alcohol with a protic acid. p-Toluenesulfonic acid and CF_3COOH each totally destroyed the starting material, whereas, HBF_4 gave the starting material back after the reaction was subjected to aqueous workup.

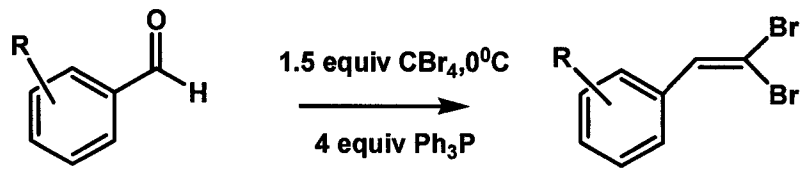
In view of the modest yields of intended [4+3] cycloaddition/nucleophilic trapping products obtained with extensive attempts at optimization, no further conditions or substrates for this process were investigated.

Conclusion:

We have demonstrated that the tandem [4+3] cycloaddition / intramolecular trapping reaction could be carried out in modest yield when a nucleophile is present within allylsilane (**96**). Attempts to optimize for the tricyclic system **101** have been performed under a variety of Lewis acids conditions, and the best Lewis acid is $B(C_6F_5)_3$

3. Benzocycloheptenynes by Intramolecular Arene Substitution Reactions of Enyne Propargyl Acetate Dicobalt Complexes

There is a need for development of new methods for the synthesis of benzocycloheptynedicobalt complexes (Section 2.1, Introduction). Our proposed route, featuring intramolecular Nicholas reaction of arenes, has been outlined in **Figure 23** (**Introduction**). In order to investigate the synthetic approach of benzocycloheptyne dicobalt complexes (**Figure 23**), a series of aldehydes have been chosen as the starting point. 2,2-Dibromo-1-alkenes **61** were prepared by a C-1 homologation of the corresponding aldehydes by a standard procedure[72] (**Scheme10**). CBr_4 is known to react with PPh_3 at 0^0C to generate dibromomethylenetriphenylphosphorane, which in turn undergoes a Wittig type reaction with aromatic aldehydes to give 2,2-dibromo-1-alkenes.



61

Scheme 10 Preparation of 2,2- dibromo-1-alkene

In all cases, the reactions went without difficulty and gave very good yields, ranging from 90% to 100%, except compound **116** (77%)(**Table 2**). Indole-3 carboxaldehyde itself was not successful in this step, as it was oxidized to pink colored material in the reaction without generating any intended product. For that reason, an N-acetyl protected indole aldehyde was employed. All products were

isolated as light green oils, except compound **116**, which was isolated as a light green solid. In order to get the dibromoalkenes in uncontaminated form, the crude reaction products have been treated with methyl iodide in petroleum ether, and then passed through a silica gel plug to remove any excess triphenyphosphium salt. Compound **116** is insoluble in petroleum ether; the clean product was therefore obtained after vacuum filtration of crude material by washing with petroleum ether. This may be the reason for the slightly lower yield of **116** than in the other cases. Some of the dibromoalkenes were not very stable in air. Compounds **113** and **114,** in particular, changed to a dark green color within 12 hours. Therefore, they were used in the next step immediately.

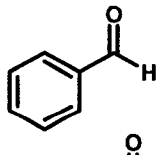
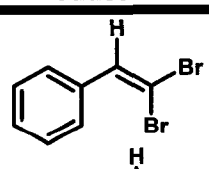
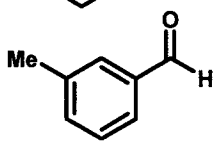
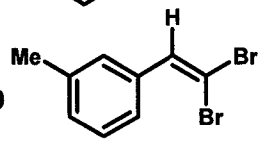
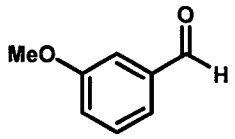
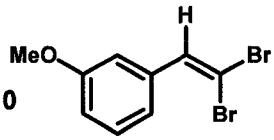
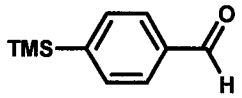
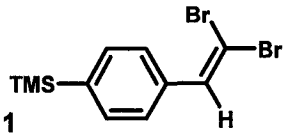
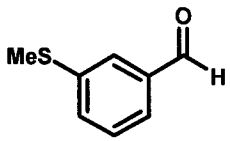
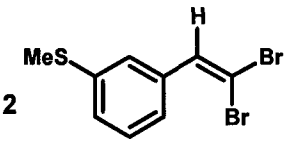
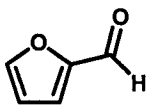
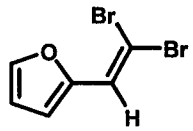
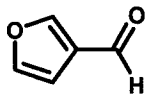
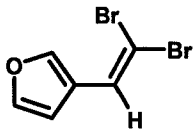
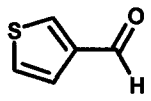
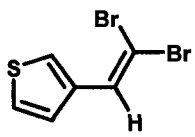
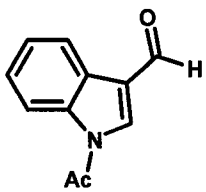
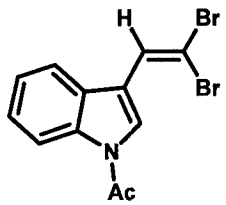
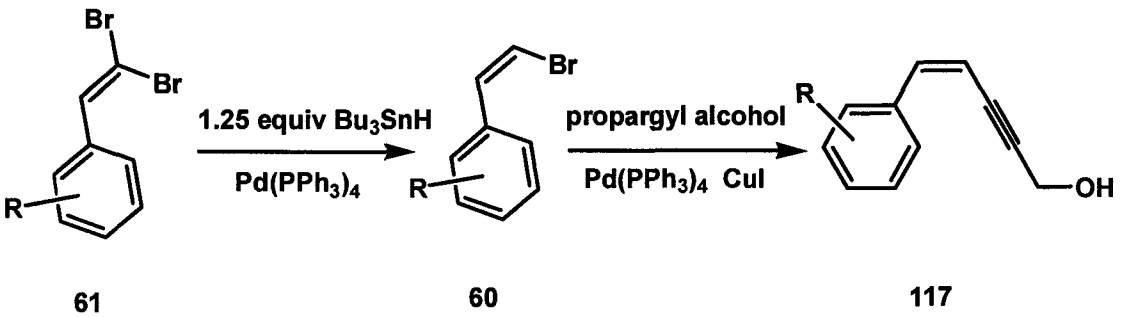
Entry	No.	Product	Yield%
	108		94
	109		92
	110		100
	111		91
	112		95
	113		93
	114		94
	115		90
	116		77

Table 2 Formation of 2,2-dibromoalkenes

In order to prepare the (Z)-enynyl alcohol, a stereoselective hydrogenolysis of the 1,1-dibromo-1-alkenes and a stereospecific synthesis of conjugated enyne compounds were necessary. The method employed was based on one published paper by Uenishi,[73] and it is shown in **Scheme 11**.



61 60 117

Scheme 11 Preparation of conjugated enyne alcohols

The high selectivity of the hydrogenolysis occurs because the oxidative addition step is the key step, where Pd(0) inserts into the less sterically hindered C-Br bond. Generally, a slight excess (1.25 equiv) of Bu_3SnH was required for clean hydrogenolysis; when further excess amounts of Bu_3SnH were used, terminal alkenes will be generated due to over hydrogenolysis. Since the Bu_3SnBr byproduct does not disturb the subsequent reaction, and the Pd(0) catalyst is still active, a Sonogashira cross coupling of **60** with propargyl alcohol in diisopropylamine solvent could be carried out in one pot, after the addition of the traditional CuI cocatalyst. One reason that the one pot route was chosen was the easier separation of the propargyl alcohol from the organotin byproduct and any retained monobromoalkene.

The results of the tandem hydrogenolysis- Sonogashira coupling are shown in **Table 3.** All the reactions were successful, yields ranging from 49% to 71%, with only compound **120** giving a slightly lower yield in comparison to the others. The products were light yellow colored oils, except compound **128**, which was a yellow solid.

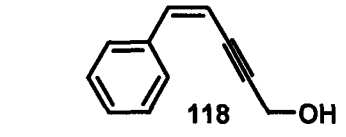
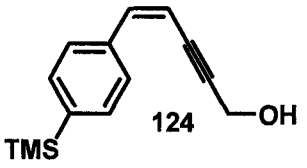
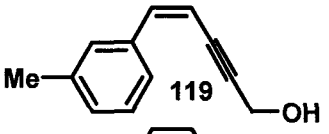
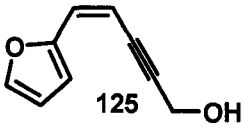
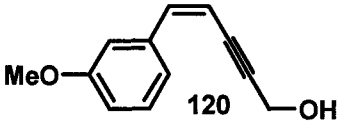
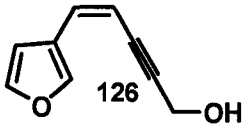
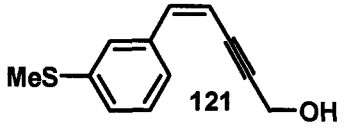
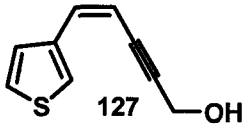
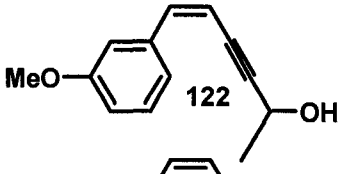
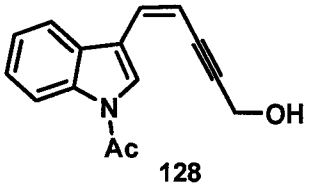
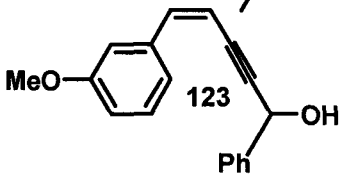
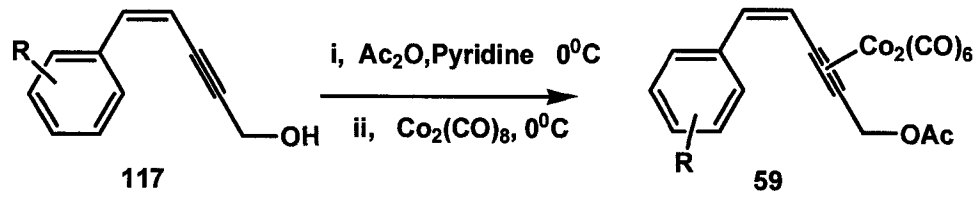
Product	Yield%	Product	Yield%
 118	71	 124	68
 119	58	 125	65
 120	49	 126	54
 121	69	 127	51
 122	90	 128	62
 123	70		

Table 3 Results of enyne alcohol syntheses

With the required alcohols in place, it simply remained to convert the enynes into cobalt complexes. Acetate leaving groups were chosen due to their greater flexibility in Nicholas reactions. To accomplish this, the alcohols were treated with acetic anhydride and pyridine to acetylate at the OH group, followed by solvent removal and complexation with $Co_2(CO)_8$ without purification of the intermediate (**Scheme 12**).The corresponding acetate complexes were isolated in good yields, ranging from 70% to 86%. (**Table 4**)



117 59

Scheme 12 Preparation of enyne acetate dicobalt complexes

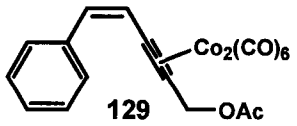
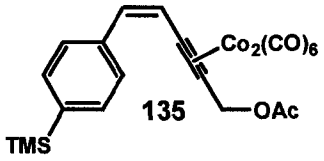
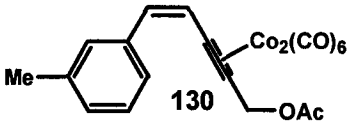
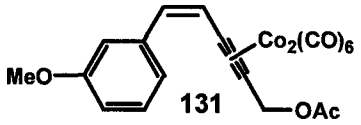
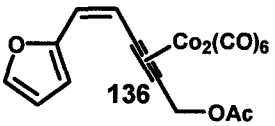
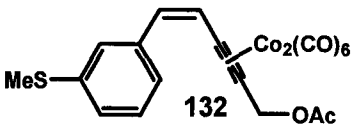
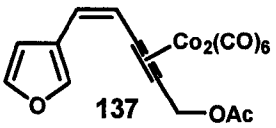
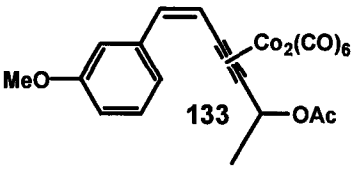
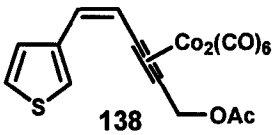
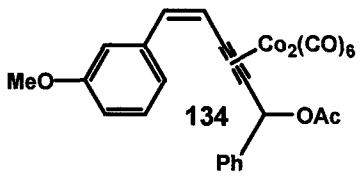
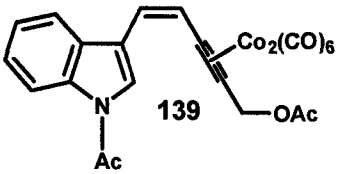
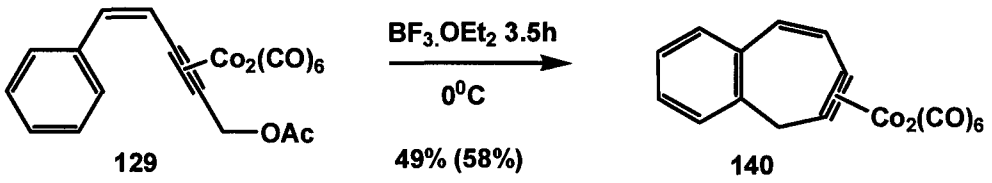
Product	Yield %	Product	Yield%
 129	80	 135	80
 130	86		
 131	76	 136	71
 132	86	 137	70
 133	70	 138	81
 134	80	 139	72

Table 4 Enyne acetate dicobalt complexes

3.1 Intramolecular Fridel-Crafts Alkylation of Enyne Acetate Dicobalt Complexes

With the precursor complexes readily prepared and in hand, the study of intramolecular Nicholas reaction could be started. $BF_3{\cdot}OEt_2$ was selected as the Lewis acid for these studies by the virtue of its modest tendency to induce decomposition in cobalt alkyne complexes.

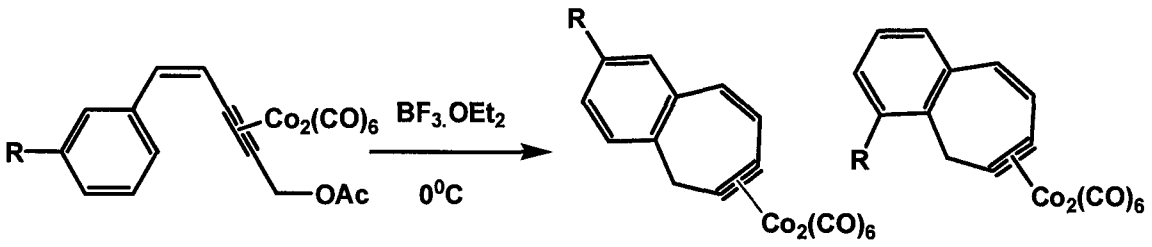


Scheme 13 Cyclization of phenyl enyne acetate dicobalt complexes

It has been reported that benzene itself usually is not a good nucleophile for Nicholas reactions, except when it has been used as solvent.[13] In **Scheme 13**, the benefit from the intramolecular nature of these Nicholas reactions is apparent. When compound **129** was treated with 3 equiv of $BF_3{\cdot}OEt_2$ at 0^0C, target product **140** was obtained in 49% yield, 58% based on recovered the starting material. Since benzene is only electronically neutral, the Friedel-Crafts reaction is slow in this case (3.5 h). The reaction was quenched before the starting **129** was completely consumed, simply because some decomposition occurred in competition with the reaction, and this became more extensive at longer reaction times.

An intermolecular reaction to give dimer or trimer compounds may also occur in the reaction during long reaction times. Additional peaks were evident around 4.0 ppm, indicative of a $[Ph\text{-}CH_2\text{-}CC]\text{-}Co_2(CO)_6$ group in ^{1}HNMR spectroscopy of crude product. By diluting the reaction concentration (0.01M), the intermolecular reactions could be decreased, with less than 2% of minor side products being observed by ^{1}HNMR spectrocopy. The remaining starting material was due to the fact that equilibrium exists between the acetate and the cobalt stabilized propargylic cation.

In the cyclization step, a protic acid could not be used, because preliminary experiments demonstrated the isomerization of the *cis* alkene to *trans* olefin in the presence of H^+.

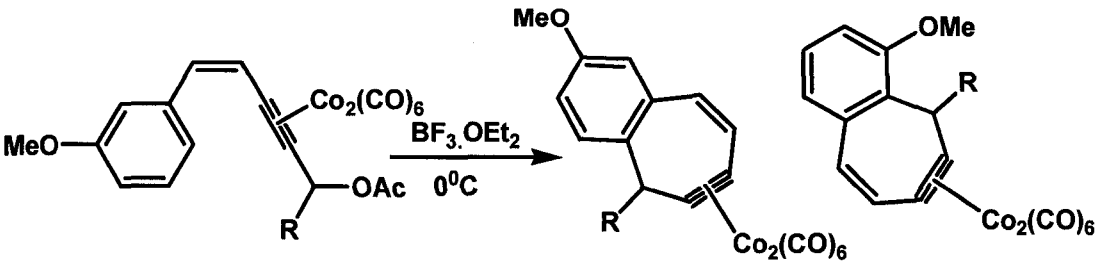


R= Me	130	67%	141a	3:1	141b
R= OMe	131	53%	142a	5:1	142b
R= SMe	132	18%	142a	4:1	143b

Scheme 14 Cyclization of substituted benzenes

For the *meta* disubstituted arenes chosen as substrates, the substituents direct to the *ortho* and *para* positions, so two regioisomers were formed in the cyclization reaction (**Scheme 14**). Methyl and methoxy group are electron donating, which make the benzene ring more electron rich. Therefore, better yields (67%, 53%) were obtained in shorter reaction times (1.5 h for **130**; 0.5 h for **131**). The ratios between the two regioisomers were 3:1 and 5:1 (*para*: *ortho*) respectively. The yield of the MeO substituted benzene (**142a** & **142b**) was a little lower than expected. During the reaction process, decomposition was the noticeable problem. Lowering the reaction temperature from 0^0C to -10^0C did not significantly increase the yield. The methylthio group may have coordinated with $BF_3{\cdot}OEt_2$ at the sulfur atom, which would deactivate the benzene ring and

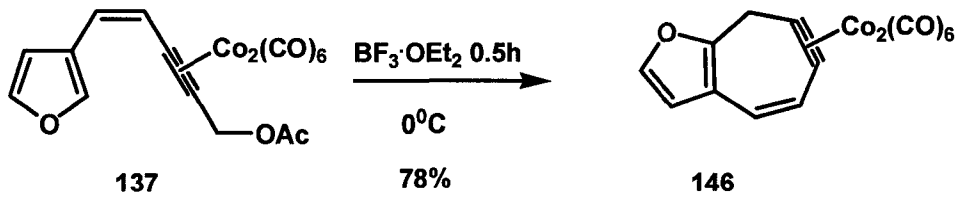
therefore be responsible for the poor yield (18%) of products and significant decomposition. The ratio of two isomers was 4: 1.



R= Me	133	77%	144a	7 : 1	144b
R= Ph	134	90%	145a	12.5 : 1	145b

Scheme 15 Substrate effect at propargyl site

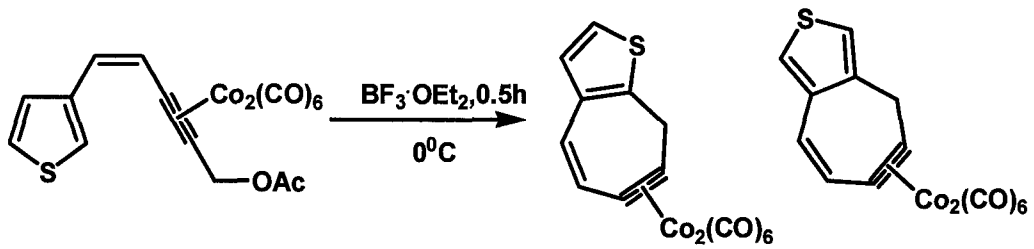
Two cases substituted at the propargyl site were investigated. In methyl-substituted case **133**, a β-hydrogen is present in the propargyl cation. This can therefore undergo elimination in competition with any Nicholas reaction process. Nevertheless, exposure of **133** to $BF_3{\cdot}OEt_2$ rapidly (0.5 h) gave complex **144** in good yield (77%), without evidence of significant β-elimination. The phenyl-substituted case **134** has no potential for β-elimination, and underwent cyclization in excellent yield (90%) in 0.5 h. (**Scheme 15**) The ratio of two regioisomers in those two cases has increased to 7:1 and 12.5:1 respectively; this could be explained by the fact that phenyl is more sterically hindered than an methyl group, which is in turn more hindered than a hydrogen atom (see **142a: 142b**).



137 78% 146

Scheme 16 Cyclization of 3-substituted furan

Electron rich heterocycles also participated in this cyclization. Treatment of compound **137** with $BF_3.OEt_2$, resulted in its complete consumption in half an hour, and a 78% yield of corresponding C-2 cyclization product **146** was obtained (**Scheme 16**).

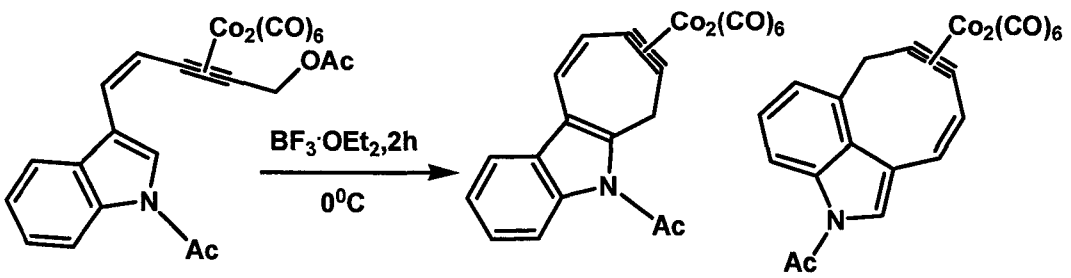


138 83% 147a 5 : 1 147b

Scheme 17 Cyclization of 3-substituted thiophene

Thiophene **138** was reacted under the same conditions as compound **137**. Surprisingly, two products, compound **147a** and compound **147b**, were obtained in total 83% yield, and in a 5:1 ratio (**Scheme 17**). The presence of C-4 product **147b** was a surprise to us; nevertheless, thiophenes are known to undergo electrophilic aromatic substitution at C-3/C-4 to a greater degree than the corresponding furans. The propargyl cation may also in fact act as an electron withdrawing group at C-3 on the thiophene ring, slightly deactivating the C-2

position for electrophilic substitution. The reactivity of C-2 and C-4 therefore is close so C-4 cyclization occurred in this reaction.[74]

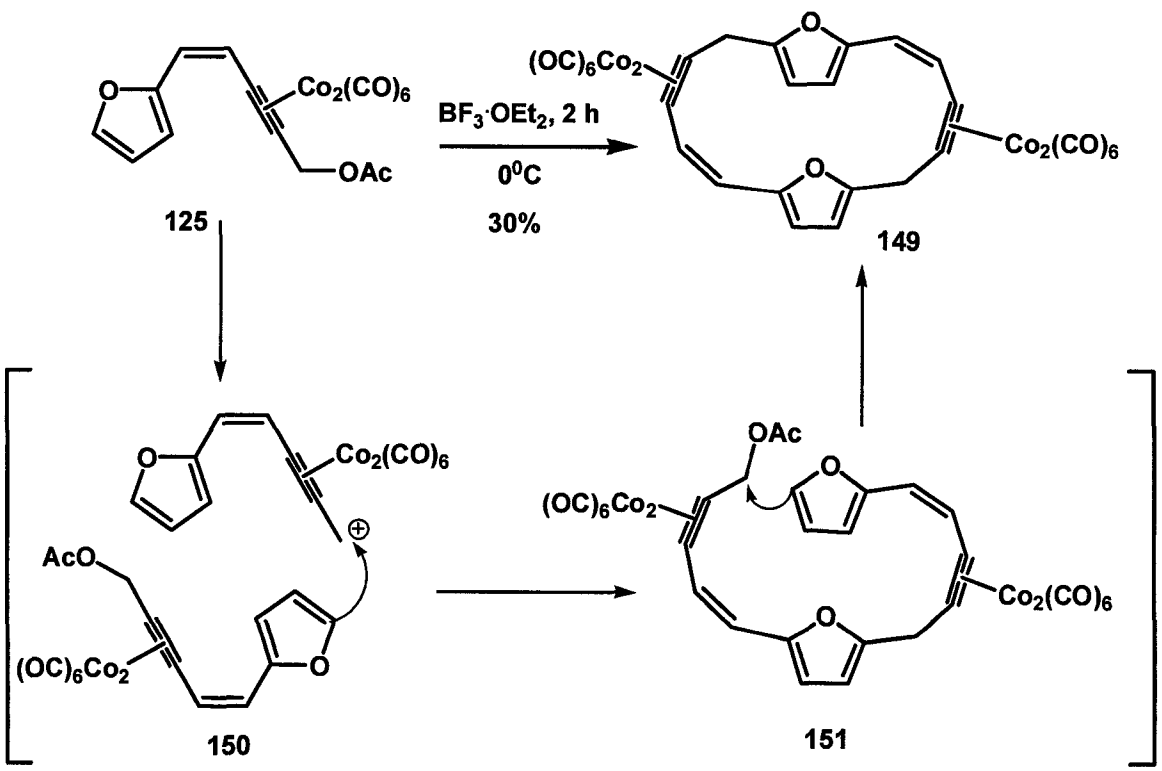


139 **148a** **148b**

38% **47%**

Scheme 18 Cyclization of 3-substituted N-acetyl-indole

A regioisomeric mixture of cyclization products was also observed with indole **139.** In addition to C-2 cyclization product **148a**, which was obtained in 38% yield, C-4 cyclization product **148b** was isolated in 47% yield (**Scheme 18**). The acetyl group on the nitrogen atom may be responsible for this, as it is a electron withdrawing group, and lowers the electron density at the C-2 position, thereby allowing the reaction to favor the C-4 position and the corresponding eight membered ring system.[75]



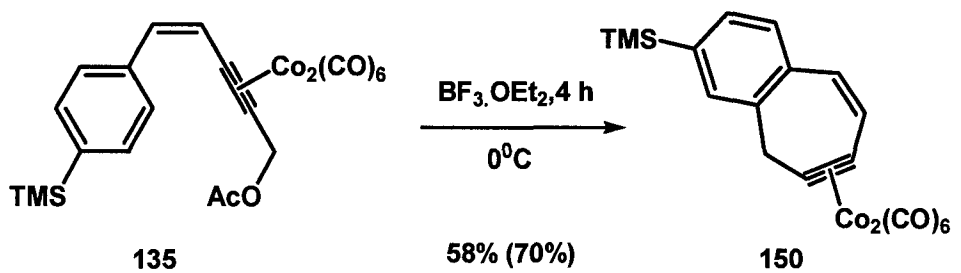
Scheme 19 Dimer formation of 2-substituted furan

In C-2 substituted furan **125**, the C-3 site has less electron density than the C-5 site. When the reaction was carried out at the same conditions as for the other substrates, a longer reaction time was required. After two hours, the only isolable material obtained was a dimeric compound **149** (**Scheme 19**). No C-3 intramolecular substitution product was observed. We belived that the double bonds in complex **149** are still in a *cis* configuration, because we have not seen any isomerization in the other cases. Nevetheless, the ^{1}H NMR coupling constant of the vinyl protons is larger than normal (J=15 Hz), and in a range traditionally associated with *trans* alkenes. An NOE NMR experiment has proven the *cis* configuration. Irradiation of the δ 7.83 resonance resulted in a 3.65% integrated

enhancement of the δ 6.63 resonance, whereas irradiation of the δ6.83 resonance resulted in a 1.62% integrated enhancement of the δ 7.83 resonance.

This source of **149** is as follows. After the propargyl cation intermediate was formed, the C-5 carbon of another molecule of **125** attacked the cation to give acyclic dimer **151**, which then cyclized through the remaining C-5 position to form dimeric molecule **149**. The yield is only 30%; this may be because of the long exposure of furan to Lewis acid, which can cause some decomposition. However, a 30% yield is consistent with the yields of several related macrocyclizations.[33]

At very low reaction concentration (0.001M), a product mixture was obtained that had spectral data consistent with the presence of a small amount C-3 and C-5 intramolecular cyclization products. In the ^{1}HNMR spectrum, additional peaks appeared at [δ 4.27(2H, s); 4.26(2H, s); 6.35(1H, d, J=11.7); 6.40(1H,d, J=9.9); 6.47(3H, m); 6.51(1H, d, J=10.1); 7.52(1H, s)]. However, these constituted a very small amount of the material that could not be separated or fully characterized.



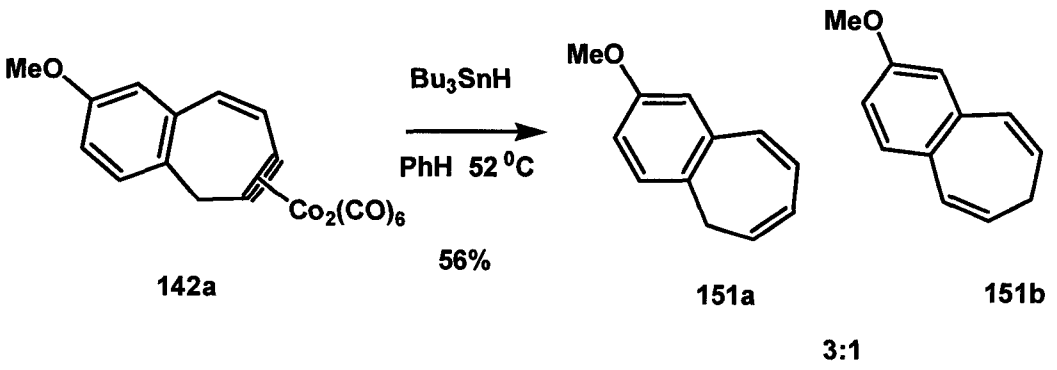
135 58% (70%) 150

Scheme 20 Cyclization of *p*-TMS benzene

As the former examples illustrate, electron-donating substituents at the *meta* positions of benzene worked most efficiently in this methodology. To expand this chemistry to a wider range of substituted benzenes, a p-trimethylsilyl case was selected as a substrate. It has several advantages: i) it is a slightly electron-donating group to make the benzene ring more reactive; ii) it is easily replaced by other functional groups to make diversely functioned benzenes; iii) the *meta* and *ortho* positions to the TMS group have similar nucleophilicities, so that dimer formation would likely not be a big problem. Upon the addition of $BF_3{\cdot}OEt_2$, the reaction proceeded very smoothly, except that the reaction time was a little longer (4 h), and it was again prudent to stop the reaction before completion. Under these conditions the desired compound **150** was obtained in 58% yield without losing the TMS group; based on recovered starting material, the yield was 70% (**Scheme 20**).

3.2 Reductive Decomplexation of a Benzocycloheptyne Complex.

As no natural products contain a dicobalt unit, the removal of the cobalt fragment to give a metal free compound is of much importance to the relevance of this work. To reach this goal, reduction of one of the cycloheptyne complexes **142a** to *cis* olefin has been carried out by employing conditions published by Isobe.[76]



Scheme 21 Decomplexation of dicobalt complexes to *cis*-olefine

When Bu_3SnH was used as the reducing reagent under the published conditions (65 ^{0}C, benzene solution), two products (**151a** & **151b)** were obtained in 40%, (**151a: 151b** =2:1). Hydrogen migration has taken place in the reduction step; this feature has been observed in some of Isobe's cases, but was rare with Bu_3SnH. Lowering the reaction temperature with Bu_3SnH to 52 ^{0}C gave an improved yield of **151** (56%) and a lower amount of isomerization product (**151a: 151b** =3:1). No expected product was obtained when NaH_2PO_2 was in use, but rather undetermined products in lower yields and consistent with an allylic alcohol. Further optimizations were not pursued due to time limitations.

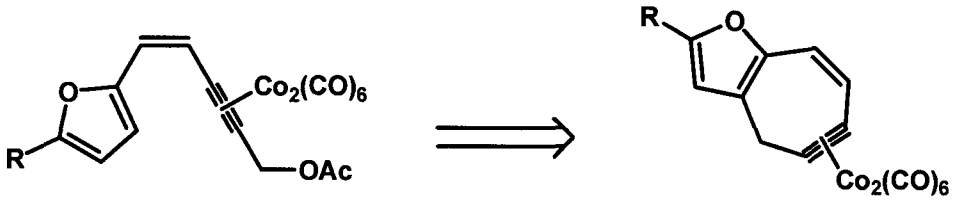
Conclusion

We have developed a novel method to synthesize benzocycloheptyne dicobalt complexes by intramolecular Nicholas reactions of enyne acetate dicobalt complexes, which have been obtained from aldehydes in a limited number of steps (**Figure 10**). In most of the cases, the target compounds have

been achieved in good yield. Reductive decomplexation of complex **142a** has produced a benzocycloheptadiene in fair yield.

Future Work

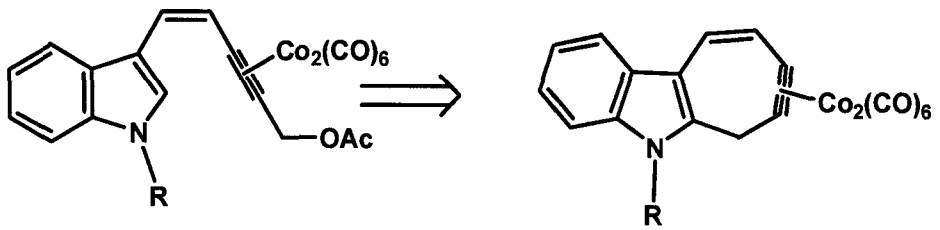
We have seen promising results for C-3 cyclization product of compound **142**. It is possible to increase the yield for the C-3 cyclization product by blocking the C-5 carbon with TMS or methyl group. (**Scheme 22**)



R= TMS or CH_3

Scheme 22 Possible C-3 cyclization of 2-subtituted furan

In the indole cyclization case, the C-4 cyclization is dominant due to the lower electron density at C-2 position induced by the electron withdrawing acetyl group at nitrogen atom. We can modify compound **139** to N-deprotect or by employing electron-donating group (such as TMS, CH_3) as the N-protecting group **152** (**Scheme 23**), the yield of intended C-2 cyclization product likely will be increased.

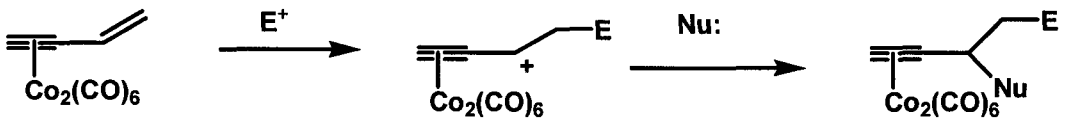


152 **153**

R=H, TMS, or CH_3

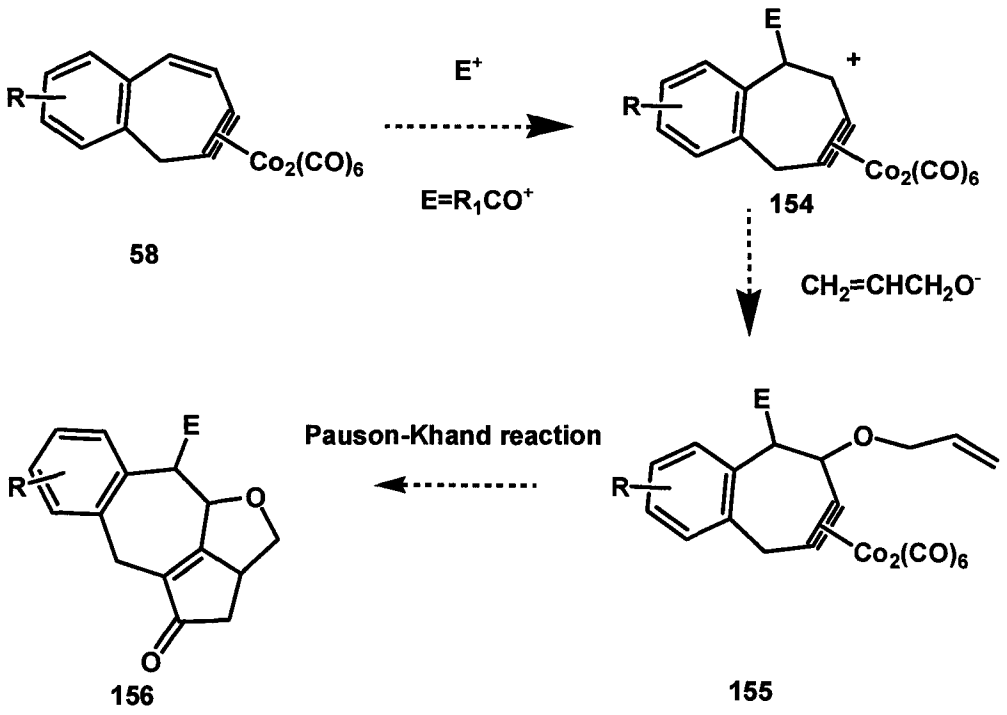
Scheme 23 Possible C-2 cyclization of indole derivatives

Smit and Caple have reported the reaction of conjugated enyne complexes with electrophiles following nucleophile trapping the propargyl cation (**Scheme 24**).[77]



Scheme 24 Electrophilic attack initialted reactions of enyne dicobalt complexes

In view of this process, the benzocycloheptyne dicobalt complexes could be used as intramolecular Pauson-Khand reaction precursors (**Scheme 25**). Electrophiles, such as acylium ion, would be attaked by the alkene to generate propargyl cation **154**, which in turn may be trapped by a nucleophile (i.e. unsaturated allyl alcohol) to give the Pauson-Khand precursor **155**. Subsequently, an intramolecular Pauson-Khand reaction could be carried out; ideally fused ring system **156** will be obtained.



Scheme 25 Possible eletrophilic attack and Pauson-Khand reaction

Experimental

General Information

All reactions have been carried out under a nitrogen atmosphere. The term "–78^{0}C" refers to the temperature of a acetone-dry ice bath; the term "–10^{0}C" refers a saturated salt ice bath, while "0^{0}C" refers to an ice water bath. A conventional "workup" means that the solutions were extracted 3 times with diethyl ether or dichloromethane after quenching the reaction with saturated sodium bicarbonate solution or saturated ammonia chloride solution, and then the organic layers were dried by magnesium sulfate; after vacuum filtration, evaporation of the solvent under reduced pressure yielded the crude products.

The solvents were utilized after purification by the "Grubbs' type" solvent purification system, which was made by Innovative Technology. Lewis acids and aldehydes were distilled before using; unless otherwise specified, all the other chemicals were used as they were received without further purification.

Analytical thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F25 sheets, while the preparative TLC was done on Aldrich silica gel GF 1000-micron plates. Flash chromatography utilizes Still's method[78] with (230-300 meso) silica gel 60 from Silicycle

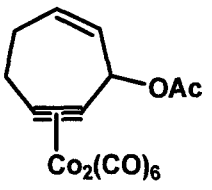
The NMR spectra were achieved by using either a Bruker Avance 500 or 300 spectrometer at 500 MHz or 300 MHz for ^{1}H and correspondings125 MHz or 75 MHz for ^{13}C, in $CDCl_3$ solution at room temperature. Chemical shifts are expressed in ppm relative to the residual chloroform resonance (7.27 ppm in $CDCl_3$), while the coupling constants are given in Hertz .Low resolution mass

spectra were recorded on Varian Saturn 1200 MS instrument in electron impact mode. FT-IR spectra were obtained from a Bruker Vector 22 FT-IR spectrometer, using KBr plates and were reported as wave number (cm^{-1}) maxima. IR absorptions are reported only selectively, for major function group stretches. The absorptions of concerned are listed in **Table 5**. High resolution mass were obtained from McMaster university.

Table 5 Important IR Stretching Frequencies

Type of Bond	Frequencies(cm^{-1})
C–H(sp^2)	3100–3000
C–H (sp^3)	3000-2800
Ph	~1600 and ~1500
C=C	1660–1500
O–H(alcohol)	3650–3200
C=O	1780-1650
M=C=O	2000-2100
C≡C	2260-2100

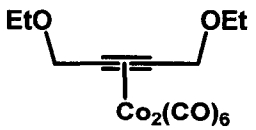
Hexacarbonyl[μ-η^4-(3-acetoxycyclohept-1-en-4-ynyl)dicobalt (Co-Co) (81)



81

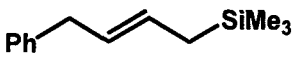
Compound **81** was synthesized by the procedure described by Green in 74% yield.[42]

Hexacarbonyl[μ-η^4-(1,4 diethoxy-2-butyne)dicobalt (Co-Co) (49)



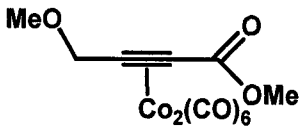
Compound **49** was prepared by the method of Patel in 80% yield. [79]

Trimethyl(4-phenylbut-2-enyl)silane (96)



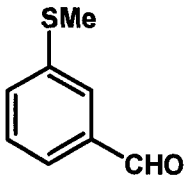
Compound **96** was prepared by the method of Tsuji in 45% yield.[71]

Hexacarbonyl[μ-η^4-(methyl 4-methoxy-2-butynoate)]dicobalt (Co-Co) (105)



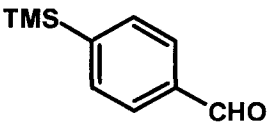
Compound **105** was prepared by the method of Mohamed and Green in 82% yield.[39]

3-(Methylthio)benzaldehyde (157)



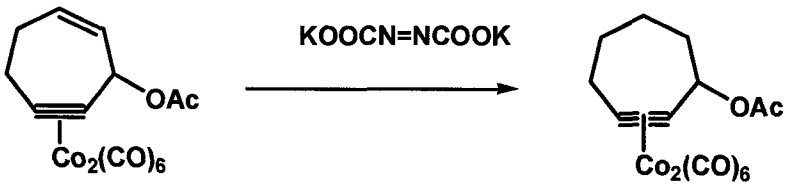
Compound **152** was prepared by the method of Waigh in 85% yield.[80]

4-Trimethylsilylbenzaldehyde (158)



Compound **158** was prepared by the method described by Narutaa. [81]

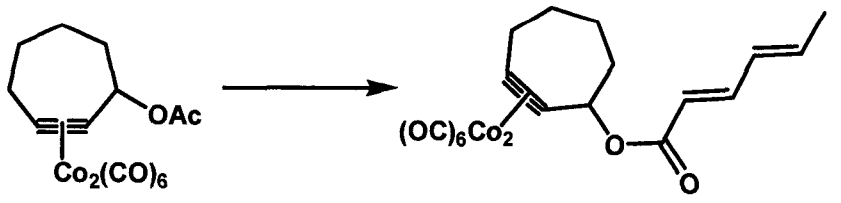
Hexacarbonyl[μ-η^4-(3-acetoxy-cycloheptyne)dicobalt (Co-Co) (81)



81 **82**

To a solution of compound **81** (164.3 mg, 0.37 mmol) in methanol (20 mL), fresh KOOCN=NCOOK (359 mg, 1.85 mmol) was added followed with acetic acid. Once evolution of gas has ceased, the procedure was repeated with monitoring by TLC. After the reaction was judged complete (*ca* 2h), the solvent was removed under reduced pressure. Saturated $NaHCO_{3\ (aq)}$ was added to the residue and the mixture was subjected to conventional workup with CH_2Cl_2. After flash chromatography (20:1 petroleum ether: diethyl ether), compound **82** was obtained in (116.3 mg, 78% yield) as red-brown oil. The spectra were identical to former report.[54]

Hexacarbonyl[μ-η^4-(hexa-2,4-dienoic acid cyclohept-2-ynyl ester)dicobalt (Co-Co) (83)

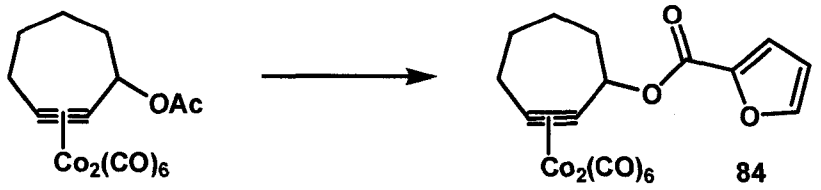


82 83

$BF_3.OEt_2$ (133 mg, 0.94 mmol) in dichloromethane (1 mL) was added over 10 minutes to compound **82** (82 mg, 0.19 mmol) and sorbic acid (210mg, 1.87mmol) in a dichloromethane (3.7 mL) solution at 0^0C. The solution was stirred for another 40 minutes, and saturated $NaHCO_{3(aq)}$ was added. After a conventional work up, the crude material was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford compound **83** (64.2 mg, 70% yield) as brown oil.

IR (neat, KBr): 2931, 2092, 2051, 2023 cm^{-1}. **^{1}H NMR**: δ 1.55(2H, m), 1.67(1H, m) 1.86(3H, d, J=6.7), 2.02(2H, m), 2.22(1H, m), 2.79(1H, m), 3.20(1H,d, J=16.5), 5.82(1H, d, J=15.4), 5.97 (1H, dd, J=10.5, 4.5), 6.16(2H, m), 7.31(1H, dd, J=15.4,10.5) **^{13}C NMR**: δ. 199.7, 166.7, 145.5, 139.6, 129.8, 118.5, 98.1, 97.7, 75.6, 35.6, 35.1, 29.2, 25.7,18.6 **MS (EI, m/z)**: 462[M-CO]$^+$, 434[M-2CO]$^+$, 406[M-3CO]$^+$, 378[M-4CO]$^+$, 350[M-5CO]$^+$, 322[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{19}H_{16}Co_2O_8$ cal: [M-CO]$^+$ 461.9560, found 461.9537.

Hexacarbonyl[μ-η^4-(furan-2-carboxylic acid cyclohept-2-ynyl ester)dicobalt (Co-Co) (84)

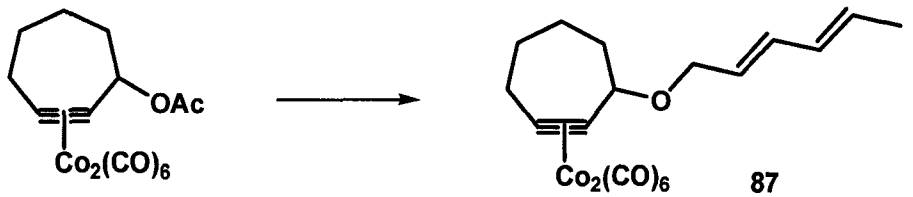


84

$BF_3.OEt_2$ (1.52 mg, 1.1 mmol) in dichloromethane (1 mL) was added to compound **82** (93.8 mg, 0.21 mmol) and 2-furoic acid (240 mg, 2.1 mmol) in dichloromethane (4.3 mL) solution over 10 minutes at 0^0C, the solution was stirred for 40 minutes, and saturated $NaHCO_{3(aq)}$ was added. After a conventional work up, the crude material was purified by flash chromatography (7:1 petroleum ether: diethyl ether) to afford compound **84** (97.8 mg, 77% yield) as brown oil.

IR (neat, KBr): 2931, 2856, 2092, 2030,1720 cm^{-1}. **^{1}H NMR**: δ 1.56(3H, m), 1.78(1H, m), 2.02(2H, m), 2.31(1H, m), 3.20(1H, m), 6.11(1H, dd, J=10.6, 4.4), 6.50(1H, s), 7.21(1H, d, J=3.4), 7.56(1H, s). **^{13}C NMR**: δ 198.9 (br), 158.3, 146.5, 144.5, 118.0, 111.8, 97.8, 97.2, 53.4, 35.6, 35.1, 29.2, 25.6. **MS (EI, m/z)**. 462[M-CO]$^+$, 434[M-2CO]$^+$, 406[M-3CO]$^+$, 378[M-4CO]$^+$, 350[M-5CO]$^+$, 322[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{18}H_{12}Co_2O_9$ cal: 433.9247 [M-2CO]$^+$ found 433.9239.

Hexacarbonyl[μ-η^4-(3-(hexa 2,4-dienyloxy)cycloheptyne)]dicobalt (Co-Co) (87)

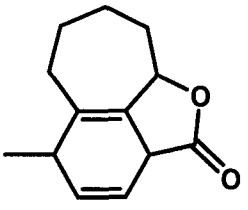


87

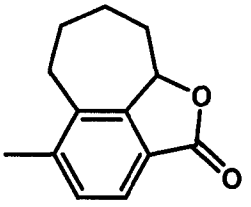
HBF_4 (0.28 mL, 2.0 mmol, 54% in diethyl ether solution) was added to the compound **82** (86.1 mg, 0.20mmol) and dimethyl sulfide (122 mg, 2.0 mmol) in diethyl ether (4 mL) solution at room temperature. The mixture was stirred for 1 h and was monitored by TLC. The volatiles were evaporated under reduced pressure. The residue was dissolved in dichloromethane, 2,4 hexadienol was added to the solution, and the mixture was stirred for another 2.5 hours. Saturated $NaHCO_{3(aq)}$ was added, and the mixture subjected to a conventional workup. The compound **87** was obtained (21.6 mg, 23% yield) as brown oil after purification by flash chromatography (10:1 petroleum ether: diethyl ether).

IR (neat, KBr): 2929, 2091, 2049, 2022, 1719 cm^{-1} **^{1}H NMR**: δ 1.56(2H, m), 1.76(3H, d, J=6.3), 1.95-2.02(3H, m), 2.16(1H, m), 2.75(1H, m), 3.18(1H, d, J=16.1), 4.19(1H, m), 4.34(1H, m), 4.47(1H, dd, J=10.0, 3.7), 5.70(2H, m), 6.06(1H, m), 6.22(1H, m). **^{13}C NMR**: δ 199.9(br), 133.3, 130.8, 130.0, 126.6, 99.6, 98.7, 80.1, 69.7, 37.0, 35.4, 29.1, 25.8, 18.1.**MS (EI, m/z):** 420$[M-2CO]^+$, 392 $[M-3CO]^+$, 364$[M-4CO]^+$, 334$[M-5CO]^+$, 306$[M-6CO]^+$.

Compounds 88 and 89



88



89

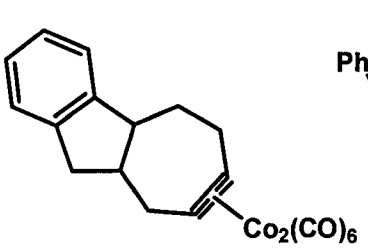
Compound **83** (104 mg, 0.21 mmol) was heated to reflux in toluene (100 mL) for 3 hours. After cooling the solution was filtered through a plug of Celite ®,

the solvent was evaporated under reduced pressure. The residue was treated with saturated ammonia chloride solution, and subjected to a conventional workup with diethyl ether, the crude material was purified by flash chromatography (5:1 petroleum ether: ethyl acetate) to afford product **88** (14.5 mg, 34% yield) as a white solid, which slowly oxidized to product **89**.

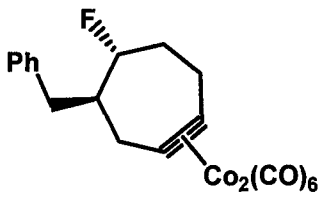
88 ^{1}HNMR: (incomplete) 1.13(3H, d, J=7.5), 5.20(1H, t. J=5.20), 5.70(1H, dd, J=9.5, 3.2), 6.20(1H, dd, J=9.5, 2.8).

89 IR (neat, KBr): 2926, 2854, 1761, 1605, 1446 cm^{-1}. **^{1}H NMR**: δ. 1.33-1.42 (3H, m), 1.79(2H, m), 2.08(1H, m), 2.11(1H, m), 2.43(3H, s), 3.19(1H, dd, J=6.6, 15.2), 5.32(1H, dd, J=3.48,12.0), 7.28(1H, d, J=7.8), 7.59(1H, d, J=7.8). **^{13}C NMR**: δ. 170.9, 151.4, 141.5, 136.3, 131.4, 123.6, 122.6, 82.4, 32.9, 29.8, 27.8, 27.1, 20.1. **MS (EI, m/z)**: 202 $[M]^+$. **HRMS (EI, m/z)** for $C_{13}H_{14}O_2$ cal: 202.0994 found. 202.0992

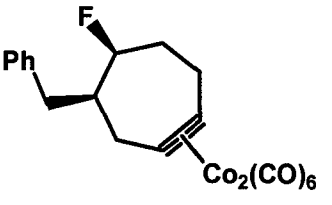
Compound 101, Hexacarbonyl[μ-η^4-(*trans*4-benzyl-5-fluoro) cycloheptyne] dicobalt (Co-Co) (102a) and Hexacarbonyl[μ-η^4-(*cis* 4-benzyl-5-chloro) cycloheptyne] dicobalt (Co-Co) (102b)



101



102a



102b

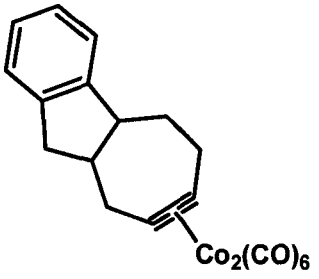
To a stirred solution of propargyl diether dicobalt complex **49** (34 mg, 0.08 mmol) and $BF_3.OEt_2$ (57 mg, 0.4 mmol) in CH_2Cl_2 (2 mL), was added compound **96** (24.5 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) solution dropwise over 1 hour at room temperature. After stirring for 1 hour, saturated $NaHCO_{3(aq)}$ was added. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether), sequentially afforded products **101, 102a and 102b** (6.8 mg, 20% yield; 10.5 mg, 27% yield; 10.5 mg, 27% yield).

101: **IR (KBr, neat):** 2924, 2080, 2046, 2018 cm^{-1}. **^{1}H NMR**: δ 1.70(1H, m), 2.36(1H, m), 2.68(1H, apparent d, J=14.1), 2.76(1H, dd, J=15.1,11.2), 2.88 (1H, t, J=10.0), 2.94(1H, dd, J=16.1,11.8), 3.03(1H, m) 3.15(1H, dd, J=8.0, 15.1) 3.40(1H, m), 3.50(1H,dd, J=3.4,16.1) 7.22(4H, m). **^{13}C NMR**: δ 200.3(br), 146.2, 142.5, 126.8, 126.4, 124.3, 123.0, 100.3, 98.3, 53.6, 51.1, 38.9, 38.7, 35.2, 34.2. **MS:(EI, m/z)** 468 $[M]^+$, 440$[M-CO]^+$, 412$[M-2CO]^+$, 384$[M-3CO]^+$, 356$[M-4CO]^+$, 328$[M-5CO]^+$, 300$[M-6CO]^+$. **HRMS** for $C_{20}H_{14}Co_2O_6$ Cal: 439.9509$[M-Co]^+$, found 439.9505.

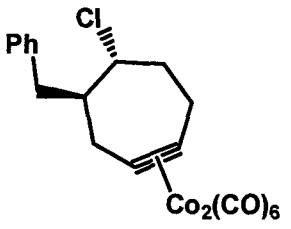
102a: **IR (KBr, neat):** 2093, 2850, 2090, 2048, 2016 cm^{-1}. **^{1}H NMR**: δ 1.62(1H, m), 2.05(1H, m), 2.40(1H, m), 2.86(2H, d, J=7.8), 3.02(3H, m), 3.10(1H, m), 4.93(1H, dd, J=44.5, 7.1), 7.19(2H, d, J=7.3), 7.25(1H, t, J=7.4), 7.33(2H, t, J=7.5). **^{13}C NMR**: δ 200.9(br), 139.5, 129.1, 128.7, 126.4, 93.7, 91.3, 65.1, 46.1, 40.6, 33.6, 29.7, 27.5. **MS:(EI, m/z)**: 488$[M]^+$, 460$[M-CO]^+$, 432$[M-2CO]^+$, 404$[M-3CO]^+$, 376$[M-4CO]^+$, 348$[M-5CO]^+$, 320$[M-6CO]^+$. **HRMS(EI,m/z):** for $C_{20}H_{15}Co_2FO_6$ cal: 319.9822$[M-6CO]^+$ found 319.9821

102b: **IR (KBr, neat):** 2923, 2850, 2090, 2047, 2016 cm^{-1}. **^{1}H NMR**: δ 2.02(1H, m), 2.43(3H, m), 2.69-2.85(2H, m), 3.05(3H, m), 4.33(1H, dt, J=44.7, 7.5), 7.24(3H, m), 7.33(2H, d, J=7.3). **^{13}CNMR**: δ 200.3(br), 139.4, 129.3, 128.5, 126.3, 93.5, 91.2, 65.1, 47.5, 33.6, 37.3, 29.7, 27.5. **MS (EI, m/z):** 488$[M]^+$, 460$[M\text{-}CO]^+$, 432$[M\text{-}2CO]^+$, 404$[M\text{-}3CO]^+$, 376$[M\text{-}4CO]^+$, 348$[M\text{-}5CO]^+$, 320$[M\text{-}6CO]^+$ **HRMS (EI, m/z)** for $C_{20}H_{15}Co_2FO_6$ cal: 319.9822$[M\text{-}6CO]^+$ found 319.9816

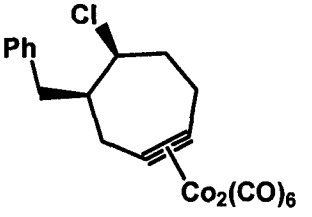
Hexacarbonyl[μ-η^4-(*trans* 4-benzyl-5-chloro)cycloheptyne]dicobalt (Co-Co) (103a) and Hexacarbonyl[μ-η^4-(*cis* 4-benzyl-5-chloro)cycloheptyne]dicobalt (Co-Co) (103b)



101



103a

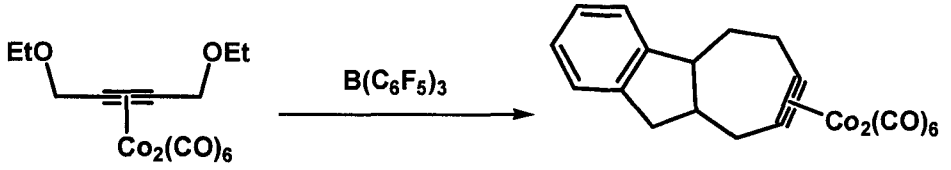


103b

To a stirred solution of propargyl diether dicobalt complexes **49** (54 mg, 0.13 mmol) and $SnCl_4$ (164 mg, 0.63 mmol) in CH_2Cl_2 (2.6 mL) was added compound **96** (40 mg, 0.19 mmol) in CH_2Cl_2 (1mL) solution dropwise over 30 minutes at room temperature. The mixture was stirred for 1 h; saturated $NaHCO_{3(aq)}$ was then added. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether), sequentially afforded product **101**, **103a** and **103b** (8.2 mg, 14% yield; 13 mg, 20% yield; 12 mg, 18% yield)

103a: **IR (KBr, neat):** 3028, 2025, 2088, 2045, 2018, 1603, 1495 cm^{-1}. **^{1}H NMR**: δ 1.8(1H, m), 2.20(1H, m), 2.28(1H, m), 2.81(2H, m), 3.1(3H, m), 3.30(1H, m), 4.4(1H, d, J=6.8), 7.21(2H, d, J=7.3), 7.24(1H, m) 7.34(2H, m). **^{13}C NMR**: δ 200.2(br), 139.2, 129.0, 128.7, 99.9, 96.8, 64.8, 47.7, 36.4, 35.9, 29.5. **MS (EI, m/z)** 504$[M]^+$, 476$[M\text{-}CO]^+$, 448$[M\text{-}2CO]^+$, 420$[M\text{-}3CO]^+$, 392$[M\text{-}4CO]^+$, 364$[M\text{-}5CO]^+$, 336$[M\text{-}6CO]^+$. **HRMS(EI, m/z):** for $C_{20}H_{15}ClCo_2O_6$ cal335.9536$[M\text{-}6CO]^+$ found 335.9513

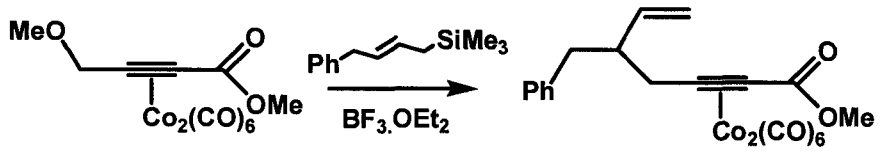
103b: **IR (KBr, neat):** 2927, 2360, 2089, 2045, 2016, 1427 cm^{-1}.**^{1}H NMR:** δ 0.86(1H, m), 1.87(1H, m), 2.27(2H, m), 2.80(2H, m), 3.09(2H, m), 3.30(1H, m) 4.49(1H, d, J=6.6), 7.27(5H, m). **^{13}CNMR:** δ199.8 (br), 139.2, 128.8, 128.7, 128.5,128.3, 98.1,96.8, 65.7, 47.9, 38.9, 33.9, 29.4. **MS (EI, m/z):** 504$[M]^+$, 476$[M\text{-}CO]^+$, 448$[M\text{-}2CO]^+$, 420$[M\text{-}3CO]^+$, 392$[M\text{-}4CO]^+$, 364$[M\text{-}5CO]^+$, 336$[M\text{-}6CO]^+$. **HRMS(EI, m/z):** for $C_{20}H_{15}ClCo_2O_6$ cal: 335.9536$[M\text{-}6CO]^+$ found 335.9501



To a solution of compound **49** (122.6 mg, 0.062 mmol) and compound **96** (19 mg, 0.093 mmol) in CH_2Cl_2 (1.2 mL) at 0 ^{0}C was slowly added $B(C_6F_5)_3$ (110 mg, 0.27 mmol) in CH_2Cl_2 (1 mL) solution over 2 hours. The mixture was stirred for an additional 2 hours at the same temperature, and then saturated $NaHCO_{3(aq)}$ was added. After a conventional workup with dichloromethane, flash

chromatography (100% petroleum ether), afforded product **101** (10.9 mg, 38 % yield)

Hexacarbonyl[μ-η^4-(methyl-5-benzylhept-6-en-2-ynoate)]dicobalt (Co-Co) (106)

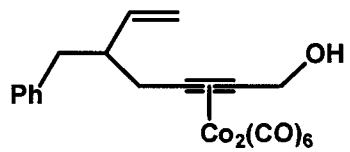


106

To a solution of compound **105** (174 mg, 0.42 mmol) and compound **96** (85.8 mg, 0.42 mmol) in CH_2Cl_2 (8.4 mL) was slowly added $BF_3.OEt_2$ (177 mg, 1.24 mmol) in CH_2Cl_2 (1 mL) solution over 30 minutes. The mixture was stirred for an additional 5h; saturated $NaHCO_{3\,(aq)}$ was then added. After a conventional workup with dichloromethane, flash chromatography (10:1 petroleum ether: diethyl ether), afforded sequential product **106** (126.2 mg, 60% yield) and recovered compound (47.3 mg, 20% yield).

IR (neat, KBr) 2926, 2099, 2062, 2028, 1710 cm^{-1}.**1HNMR:** δ 2.62(1H, m), 2.77(2H, m), 2.98(2H, m), 3.81(3H, s), 4.99(1H, d, J=17.3) 5.05(1H, d, J=10.5), 5.75(1H, m), 7.26(5H, m). **^{13}CNMR:** δ 198.3(br), 170.6, 140.8, 139.3, 129.2, 128.3, 126.2, 116.5, 98.0, 97.3, 52.9, 47.0, 42.2, 38.7, 19.4. **MS(EI, m/z):** 430[M-3CO]+, 402[M-4CO]+, 374[M-5CO]+, 346[M-6CO]+.

Hexacarbonyl[μ-η^4-(5-benzylhept-6-en-2-yn-1-ol)]dicobalt (Co-Co) (107)

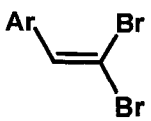


107

To a solution of compound **106** (124 mg, 0.24 mmol) in dichloromethane (4.8 mL), was slowly added DIBAL-H (0.1 mL, 2.5 M solution in toluene) at –78 ^{0}C over 30 minutes. After stirring for 2 hours at –78 ^{0}C, 1 M HCl solution was added; after a conventional work up, the crude product was purified by flash chromatography (3:1 petroleum ether: diethyl ether) to afford compound **107** (93.5 mg, 83% yield) as brown oil.

IR(Neat, KBr), 3443, 2924, 2090, 2049, 2018 cm^{-1}. **^{1}HNMR**: δ 1.84(1H, t, J=6.4), 2.64(1H, m) 2.76(2H,m) 2.97(1H, d, J=9.6), 3.03(1H, d, J=3.5), 4.73(2H, d, J=7.3), 5.03(1H, d, J=17.3), 5.12(1H, d, J=10.2), 5.80(1H, m), 7.18(3H, m), 7.30(2H,m). **^{13}CNMR:** 199.6(br), 141.4, 139.2, 129.2, 128.3, 126.3,116.6, 97.5, 95.4, 63.6, 47.5, 42.5, 39.7. **MS(EI,m/z):** 402[M-3CO]$^+$, 374[M-4CO]$^+$, 346[M-5CO]$^+$, 318[M-6CO]$^+$

2,2 Dibromo-1-alkene

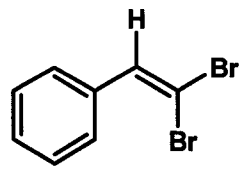


General Procedure A:

To an ice cold stirred solution of the aldehyde (1.0 mmol) and carbon tetrabromide (0.5 g, 1.5 mmol) in anhydrous CH_2Cl_2 (*ca* 10 mL) was added

triphenylphosphine (1.05 g, 4.0 mmol) in several portions. The reaction was monitored by TLC. After the reaction was complete (2-4h), the mixture was diluted with hexanes (100 mL), and filtered through silica gel using hexanes as an eluent. Removal of the solvent under reduced pressure gave crude materials. The crude product was dissolve in petroleum ether and iodomethane (excess) was added. After stirring for 30 min, the mixture was filtered through silica gel again to remove the phosphonium salt and the solvent was removed under reduced pressure to give a material of sufficient purity for subsequent use.

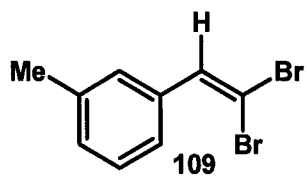
(2,2-Dibromoethenyl)benzene (108)



108

A solution of benzaldehyde (1.03 g, 9.71 mmol) in CH_2Cl_2 (50 mL) was subject to **procedure A**, to afford product **108** (2.40 g, 9.16 mmol, 94% yield) as light green oil. The spectroscopic data were identical to a former report. [67]

1-(2,2-Dibromo-ethenyl)3-methyl-benzene (109)

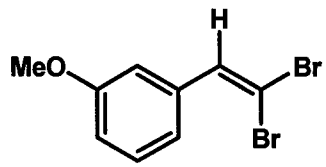


109

A solution of 3-methylbenzaldehyde (0.53 g, 4.39 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure A**, to afford product **109** (1.11 g, 92 % yield) as green oil.

IR (neat,KBr): 3013, 2919, 1603, 1056 cm^{-1}. **^{1}H NMR:** δ 2.39(3H, s), 7.16(1H, d, J=7.52), 7.26 (1H, t, J=4.5), 7.33 (1H, s), 7.36 (1H, d, J=7.8), 7.47(1H, s). **^{13}C NMR**: δ 138.1, 137.0, 135.3, 129.3, 129.0, 128.3, 125.4, 89.3, 21.4. **MS: (EI, m/z)**: 276.0.

1-(2,2-Dibromo-ethenyl)-3-methoxybenzene (110)

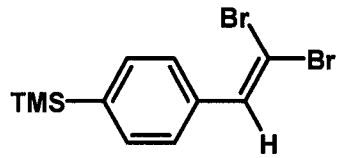


110

A solution of m-anisaldehyde (1.0 g, 7.34 mmol) in CH_2Cl_2 (50 mL) was subjected to **procedure A**, to afford product **110** (2.13 g, 100 % yield) as green oil.

IR (neat, KBr): 3384, 2926, 1598, 1576, 1480 cm^{-1}. **^{1}H NMR:** δ 3.81 (3H, s), 6.88 (1H, dd, J=7.52, 2.56), 7.08(1H,d, J=7.5), 7.11 (1H, t, J=1.79), 7.25 (1H, dd, J=15.9, 7.9), 7.45 (1H,s). **^{13}C NMR**: δ 159.4, 136.7, 136.5, 129.4, 121.0, 114.3, 113.6, 89.8, 55.3 **MS: (EI, m/z):** 292.

(2,2-Dibromoethenyl)-3-trimethylsilylbenzene(111)

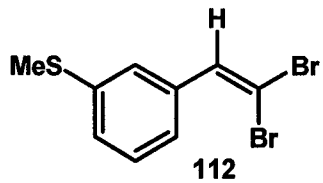


111

A solution of 4-Trimethylsilylbenzaldehyde **190** (0.73 g, 4.09 mmol) in CH_2Cl_2 (30 mL) was subjected to **procedure A**, to afford product **111** (1.25 g, 91% yield) as green oil.

IR (neat, KBr): 3013, 2955, 1598, 1248,1109 cm^{-1}. **^{1}H NMR**: δ 0.31(9H, s), 7.50(1H, s), 7.55 (4H, s). **^{13}C NMR**: δ 141.5, 136.9, 135.6, 133.3, 127.5, 89.6, −1.22. **MS (EI, m/z)**: 334.

1-(2,2-Dibromoethenyl)-3-methylthiobenzene (112)

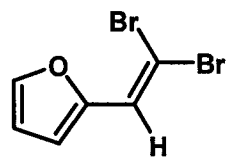


112

A solution of compound **147** (0.50 g, 3.31 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure A**, to afford product **112** (970 mg, 95 % yield) as a green oil.

IR (neat, KBr): 2919, 2851, 1587, 1562, 1470, 1437. **^{1}H NMR**: δ 2.51(3H, s), 7.24(1H, d, J=3.4), 7.29(2H, d, J=4.9), 7.43 (1H, s), 7.46 (1H, s). **^{13}C NMR**: δ 138.9, 136.4, 135.8, 128.7, 126.5, 126.0, 125.0, 90.3, 15.7. **MS (EI, m/z)**: 308.

2-(2,2-Dibromo-ethenyl)furan (113)

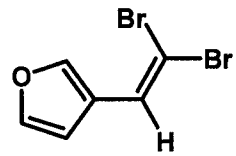


113

A solution 2-furaldehyde (1.0 g, 10.4 mmol) in CH_2Cl_2; was subjected to **procedure A**, to afford the compound **113** (2.4 g, 9.52 mmol, 93% yield) as green oil.

IR (neat,KBr): 3147, 3031, 1482, 1142 cm^{-1}. **^{1}H NMR**: δ. 6.43(1H, s), 6.96(1H, d, J=3.5), 7.42 (1H, s), 7.45 (1H, s). **^{13}C NMR**: δ 149.9, 142.4, 126.4, 111.5, 111.4, 87.1. **MS (EI, m/z)**: 252.

3-(2,2-Dibromoethenyl)furan (114)

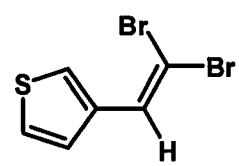


114

A solution of 3-furaldehdye (1.03 g, 10.7 mmol) in CH_2Cl_2 (50 mL) was subjected to **procedure A**, to afford product **114** (2.52 g, 94 % yield) as green oil.

IR (neat,KBr): 3023, 2925, 2853, 1573 cm^{-1} **^{1}H NMR**: δ 6.79(1H, d, J=1.25), 7.28(1H, d, J=5.64), 7.41 (1H, s), 7.83 (1H, s). **^{13}C NMR**: δ 142.9, 142.6, 128.1, 121.7, 109.6, 88.0. **MS (EI, m/z):** 252.

3-(2,2-Dibromo-ethenyl)thiophene (115)

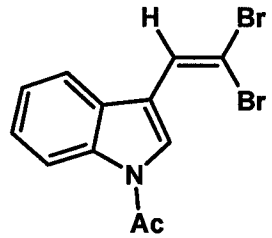


115

A solution of 3-thiophenecarboxaldehyde (0.63 g, 5.61 mmol) in CH_2Cl_2 (30 mL) was subjected to **procedure A**, to afford product **115** (1.35 g, 90 % yield) as green oil.

IR (neat,KBr): 3102, 2955, 2924, 1591, 1459 cm^{-1}. **^{1}H NMR**: δ 7.32(1H,t, J=2.07), 7.40(1H,d, J=4.69), 7.49 (1H,s), 7.70 (1H, s). **^{13}C NMR**: δ 136.0, 131.4, 127.5, 125.5, 125.2, 88.4. **MS (EI, m/z):** 268

1-Acetyl-3- (2,2-Dibromoethenyl)-indole (116)



116

To a solution of N-acetyl-3-indolecarboxaldehyde (0.69 g, 3.67 mmol) and carbon tetrabromide (1.83 g, 5.51mmol) in CH_2Cl_2 (25 mL) was added triphenylphosphine (3.86 g, 14.7 mmol) in several portions. The mixture was stirred for 3 h with monitoring by TLC. Hexanes (50 mL) were added to the solution, which was then filtered through silica gel. After removal of the solvent under reduced pressure, the petroleum ether was added, and the mixture was filtered under vacuum and washed with petroleum ether, and the solid was allowed to dry. Product **116** was obtained (970 mg, 77% yield) as a green powder.

IR (neat, KBr): 3017, 1711, 1587, 1548, 1452 cm^{-1}. **^{1}H NMR**: δ 2.65(3H, s), 7.32(1H, t, J=7.2), 7.4 (1H, t, J=7.0), 7.53 (1H, d, J=7.4), 7.58 (1H, s), 8.12(1H,

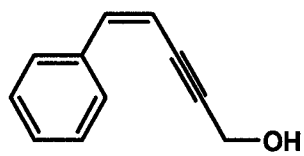
s), 8.42(1H, d, J=7.5). **^{13}C NMR**: δ. 168.5, 134.8, 129.0, 127.1, 125.9, 123.9, 123.9, 118.1, 117.1, 116.1, 89.7, 23.9. **MS (EI, m/z)**: 343.

Z-Conjugate Enynyl Alcohols

General Procedure B:

Tributyltin hydride (1.25 mmol) was added to a mixture of the 1,1-dibromo-1-alkene (1.0 mmol) and $Pd(PPh_3)_4$ (0.04 mmol) in CH_2Cl_2 (20 mL) solution at room temperature. The mixture was stirred until disappearance of the starting material was complete as monitored by ^{1}H NMR spectroscopy of a small aliquot (usually 30 minutes). After evaporation of the solvent under reduced pressure, the residue was dissolved in diisopropylamine (20 mL), and a catalytic amount CuI and propargyl alcohol (1.2 mmol) were added. The mixture was stirred for 6–12 h. A conventional workup afforded the crude reaction product.

5-Phenylpent-4-en-2-yn-1-ol (118)



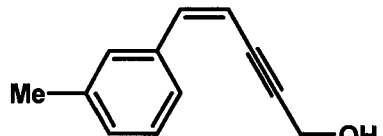
118

A solution of compound **108** (1.01g, 3.86mmol) was dissolved in CH_2Cl_2 (25 mL) was subjected to procedure **B**. The crude product was purified by flash

chromatography (10:1 petroleum ether: diethyl ether) to obtain pure compound **118** (431.6 mg, 2.72 mmol, 71% yield) as a yellow oil.

IR (neat, KBr): 3380, 2924, 2855, 2190, 1448 cm^{-1}. **^{1}H NMR**: δ 1.80 (1H, br), 4.43(2H, d, J=4.95), 5.66(1H, d, J=11.9), 6.58(1H, d, J=11.9), 7.27 (3H, m), 7.76 (2H, d, J=8.5). **^{13}C NMR**: δ 139.2, 136.2, 128.6, 128.3, 106.7, 93.8, 84.1, 51.8. **MS (EI, m/z)**: 158. **HRMS (EI, m/z)** for $C_{11}H_{10}O$ cal: 158.0732 found 158.0717.

5-(3-Methylphenyl)pent-4-en-2-yn-1-ol (119)

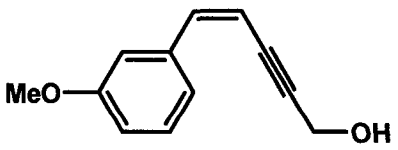


119

A solution of compound **109** (0.58 g, 2.11 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtain pure compound **119** (209 mg, 1.21 mmol, 58% yield) as a yellow oil.

IR (neat, KBr): 3345, 3020, 2920, 2861, 2193 cm^{-1}. **^{1}H NMR**: δ 1.77(1H, br), 2.38 (3H, s), 4.50(1H, d, J=1.86), 5.71(1H, dt, J=11.9, 2.0), 6.64 (1H, d, J=11.9), 7.11 (1H, d, J=7.52), 7.27(1H, d, J=10.2, 7.67), 7.63 (1H, s), 7.68 (1H, s), 7.68 (1H, d, J=7.72). **^{13}C NMR**: δ 139.4, 137.8, 136.1, 129.4, 128.2, 125.6, 106.5, 93.6, 84.3, 51.8, 21.4. **MS (EI, m/z)**: 172. **HRMS (EI, m/z)** for $C_{12}H_{12}O$ cal: 172.0888, found 172.0888.

5-(3-Methoxyphenyl)pent-4-en-2-yn-1-ol (120)

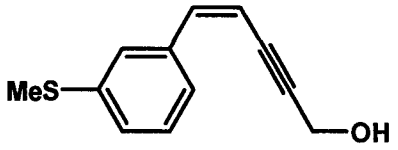


120

A solution of compound **110** (1.86 g, 6.38 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (7:1 petroleum ether: diethyl ether) to obtain pure compound **120** (600 mg, 3.19 mmol, 50% yield) as a yellow oil.

IR (neat, KBr): 3396, 2935, 2194, 1596 cm^{-1}. **^{1}H NMR**: δ 3.81 (3H, s), 4.48(2H, s), 5.70(1H, d, J=11.9), 6.60 (1H, d, J=11.9), 6.85 (1H, dd, J=7.0, 2.3), 7.26(2H, d, J=7.0), 7.63 (1H, d, J=0.76). **^{13}C NMR**: δ 159.3, 139.0, 137.4, 129.2, 114.7, 113.1, 106.9, 94.3, 83.9, 55.2, 51.7. **MS (EI, m/z)**: 188.

5-(3-Methylthiophenyl)pent-4-en-2-yn-1-ol (121)



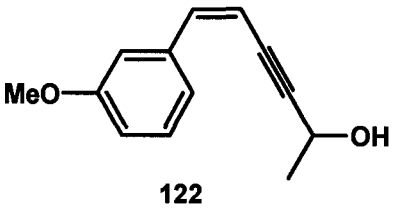
121

A solution of compound **112** (0.51 g, 1.64 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtain pure compound **121** (230 mg, 1.12 mmol, 69% yield) as a yellow oil.

IR (neat, KBr): 3372, 2920, 2857, 2190, 1585, 1560 cm^{-1}. **^{1}H NMR**: δ 2.09(1H, s), 2.50(3H, s), 4.49(2H, d, J=1.9), 5.73(1H, d, J=11.9), 6.60 (1H, d,

J=11.9), 7.20 (1H, d, J=7.83), 7.27(1H, m), 7.50 (1H, d, J=7.6), 7.86(1H, s). **^{13}C NMR**: δ 138.6, 138.4, 136.7, 128.6, 126.7, 126.0, 125.5, 107.3, 94.3, 84.0, 51.7, 15.7. **MS (EI, m/z)**: 204. **HRMS (EI, m/z)** for $C_{12}H_{12}OS$ cal: 204.0609, found 204.0607.

6-(3-Methoxyphenyl)hex-5-en-3-yn-2-ol (122)

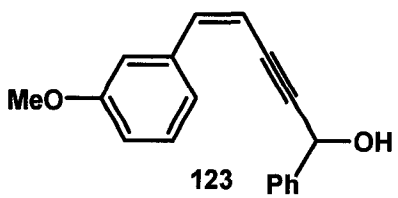


122

A solution of compound **110** (0.57 g, 1.98 mmol) in CH_2Cl_2 (25 mL), was subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtained pure compound **122** (362 mg, 1.79 mmol, 90% yield) as a yellow oil.

IR (neat, KBr): 3407, 2957, 2931, 2207, 1596, 1574 cm^{-1}. **^{1}H NMR**: δ 1.55(3H, d, J=4.3), 3.80(3H, s), 4.76 (1H, q, J=1.7), 5.72(1H, d, J=11.9), 6.60(1H, d, J=11.9), 6.88(1H, d, J=7.81), 7.28(2H, m), 7.56(1H, s). **^{13}C NMR**: δ 159.3, 138.8, 137.5, 129.1, 121.6, 114.6, 113.1, 106.9, 97.9, 82.4, 58.9, 55.2, 24.1. **MS (EI, m/z):** 202.

5-(3-Methoxyphenyl)-1-phenylpent-4-en-2-yn-1-ol (123)

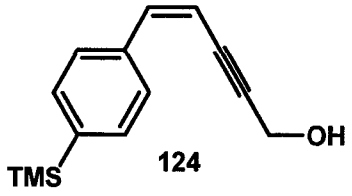


123

A solution of compound **110** (0.57 g, 1.99 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtained pure compound **123** (365 mg, 1.38 mmol, 70% yield) as a yellow oil.

IR (neat, KBr): 3425, 2925, 2168, 1636, 1594, 1575 cm^{-1}. **^{1}H NMR**: δ 2.26(1H, s), 3.70(3H, s), 5.70(1H, s), 5.80(1H, d, J=11.9), 6.68(1H, d, J=11.9), 6.86(1H, d, J=2.3), 7.23(1H, t, J=7.9), 7.35(1H, d, J=7.2), 7.40(2H, t, J=7.0), 7.52(1H, s), 7.59(2H, d, J=7.3) **^{13}C NMR**: δ 159.4, 140.4, 139.4, 137.4, 129.2, 128.6, 128.4, 126.7, 121.6, 115.0, 112.9, 106.8, 95.6, 84.9, 65.3, 55.1. **MS (EI, m/z):** 264. **HRMS (EI, m/z)** for $C_{18}H_{16}O_2$ cal: 264.1150, found 264.1138

5-(4-Trimethylsilylphenyl)pent-4-en-2-yn-1-ol (124)



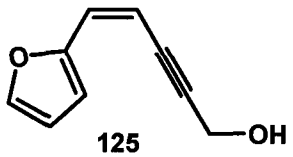
124

A solution of compound **111** (0.58 g, 1.74 mmol) was dissolved in CH_2Cl_2 (25 mL) and subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtained pure compound **124** (273 mg, 1.18 mmol, 68% yield) as a yellow oil.

IR (neat, KBr): 3443, 2955, 2188, 1640. **^{1}H NMR**: δ 0.28(9H, s), 4.52(2H, d, J=2.2), 5.72(1H, d, J=11.9), 6.65(1H, d, J=11.9), 7.53(2H, d, J=8.0), 7.81(2H, d, J=8.0). **^{13}C NMR**: δ 141.4, 139.1, 136.4, 133.2, 127.7, 106.9, 94.0, 84.0, 51.7, -

1.26. **MS (EI, m/z):** 230 **HRMS (EI, m/z)** for $C_{14}H_{18}OSi$ cal: 230.1127, found 230.1138.

5-(2-Furyl)pent-4-en-2-yn-1-ol (125)

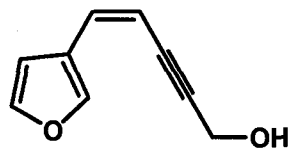


125

A solution of compound **113** (0.46 g, 1.83 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (7:1 petroleum ether: diethyl ether) to obtain pure compound **125** (176 mg, 1.18 mmol, 65% yield) as yellow oil.

IR (neat, KBr): 3374, 2958, 2927, 2197, 1464 cm^{-1}. **^{1}H NMR**: δ 1.73(1H, br), 4.55(2H, d, J=2.20), 5.56(1H, d, J=11.9), 6.47(1H, dd, J=3.1, 2.0), 6.60(1H, d, J=11.9), 7.04(1H, d, J=3.4), 7.42(1H, d, J=1.4) **^{13}C NMR**: δ152.3, 142.2, 127.5, 111.8, 111.0, 103.8, 94.1, 84.2, 51.9. **MS (EI, m/z):** 148.

5-(3-Furyl)pent-4-en-2-yn-1-ol (126)



126

A solution of compound **114** (1.03 g, 4.05 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash

chromatography (7:1 petroleum ether: diethyl ether) to obtained pure compound **126** (322 mg, 2.18 mmol, 54% yield) as yellow oil.

IR (neat, KBr): 3345, 2923, 2201, 1622, 1503, 1357, 1216. **^{1}H NMR**: δ 1.80(1H, s), 4.52(2H,s), 5.59(1H, dt, J=11.5, 2.0), 6.53(1H, d, J=11.5), 6.99(1H, s), 7.40(1H, s), 7.81(1H, s) **^{13}C NMR**: δ 143.0, 129.8, 123.2, 109.8, 105.7, 94.0, 84.4, 51.8. **MS (EI, m/z):** 148. **HRMS (EI, m/z)** for $C_9H_8O_2$ cal: 148.0524, found 148.0512

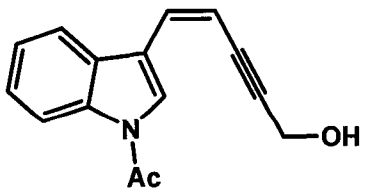
5-(3-Thienyl)pent-4-en-2-yn-1-ol (127)

127

A solution of compound **115** (0.53 g, 1.99 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtained pure compound **127** (164 mg, 1.00 mmol, 71% yield) as yellow oil.

IR (neat, KBr): 3358, 3097, 2918, 2861, 2191, 1699, 1602, 1420, 1351, 1260 cm^{-1}. **^{1}H NMR**: δ 2.39(1H, s), 4.51(2H, d, J=2.0), 5.62(1H, dt, J=11.7, 2.3), 6.70(1H, d, J=11.7), 7.29(1H, dd, J=4.9, 2.55), 7.62(1H, d, J=5.0), 7.76(1H, d, J=2.1). **^{13}C NMR**: δ 138.3, 133.0, 127.7, 125.6, 125.2, 105.2, 93.8, 84.4, 51.6. **MS (EI, m/z):** 164. **HRMS (EI, m/z)** for C_9H_8OS cal: 164.0296, found 164.0292

5-(1-Acetylindole-3-yl)pent-4-en-2yn-1-ol (128)

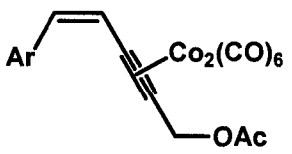


128

A solution of compound **116** (0.60 g, 1.75 mmol) in CH_2Cl_2 (25 mL) was subjected to **procedure B**. The crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) followed by fitration under vacuum and washing with petroleum ether to obtain pure compound **128** (277 mg, 1.09 mmol, 62% yield) as a yellow solid.

IR (neat, KBr): 3450, 2187, 1639, 1449 cm^{-1}. **^{1}H NMR**: δ. 2.69(3H, s), 4.59(2H,s), 5.78(1H, d, J=11.4), 6.93(1H, d, J=11.5), 7.33(1H, t, J=7.4), 7.37(1H, t, J=7.2), 7.63(1H, d, J=8.45(1H, d, J=7.9), 8.55(1H, s) **^{13}C NMR**: δ. 169.1, 135.1, 129.6, 128.8, 125.6, 124.7, 123.8, 118.3, 118.2, 116.7, 106.3, 96.0, 85.5, 51.9, 23.9. **MS (EI, m/z)**. 239 **HRMS (EI, m/z)** for $C_{15}H_{13}NO_2$ cal: 239.0946 found 239.0959.

Z –Conjugate Enyne Acetate Dicobalt Complexes

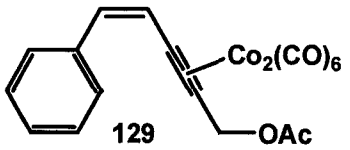


General procedure C:

To an ice cold solution of enyne alcohol (1.0 mmol) in CH_2Cl_2 (20 mL), was added acetic anhydride (excess) and pyridine (excess), the solution was

stirred until starting material consumption was judged complete (about 30 minutes to 2 h) as judged by 1H NMR spectroscopy of a small aliquot. Evaporation of the solvent and volatile side products under reduced pressure was followed by dissolution the residue in dichloromethane (20 mL), octacarbonyldicobalt (excess) was added at 0^0C, and the mixture was stirred with monitoring by TLC. After 2h, evaporation of the solvent afforded brown colored crude material.

Hexacarbonyl[μ-η^4-(1-acetoxy-5-phenylpent-4-en-2-yne)]dicobalt (Co-Co) (129)

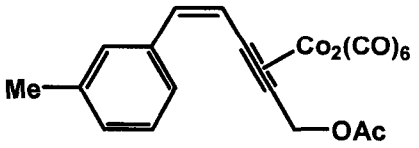


129

A solution of compound **118** (243.6 mg, 1.54 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **129** (598.5 mg, 1.23 mmol, 80% yield) as a brown oil.

IR (neat, KBr): 2361, 2092, 2023, 1747, 1393, 1217, 1029 cm^{-1}. **^{1}H NMR**: δ 202 (3H, s), 4.52(2H, s), 6.64(1H, d, J=11.1), 6.83 (1H, d, J=11.1), 7.23(2H, d, J=7.4), 7.33(1H, m), 7.41(2H, m). **^{13}C NMR**: δ 199.1(br), 170.4, 137.7, 132.4, 128.5, 128.4, 127.8, 91.5, 83.4, 64.6, 20.3. **MS (EI, m/z):** 458$[M-CO]^+$, 430$[M-2CO]^+$, 402$[M-3CO]^+$, 374$[M-4CO]^+$, 346$[M-5CO]^+$, 318$[M-6CO]^+$. **HRMS (EI, m/z)** for $C_{19}H_{12}Co_2O_8$ cal: 457.9247$[M-CO]^+$, found 457.9239

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(3-methylphenyl)pent-4-en-2-yne)]dicobalt (Co-Co) (130)

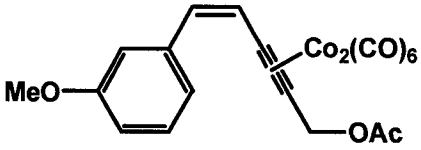


130

A solution of compound **119** (106 mg, 0.62 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **130** (264 mg, 0.53 mmol, 86% yield) as a brown oil.

IR (neat, KBr): 3014, 2927, 2092, 2024, 1748, 1373, 1217, 1029 cm^{-1}. **^{1}H NMR**: δ 2.03 (3H, s), 2.39(3H, s), 4.52(2H, s), 6.61(1H, d, J=11.0), 6.80 (1H, d, J=11.0), 7.02(2H, d, J=8.2), 7.14(1H, d, J=7.6), 7.29(1H, d, J=7.5). **^{13}C NMR**: δ 199.1(br), 170.5, 138.2, 137.6, 132.5, 129.0, 128.5, 128.4, 127.5, 125.4, 91.4, 83.5, 64.9, 21.3, 20.3. **MS (EI, m/z)**: 472[M-CO]$^+$, 444[M-2CO]$^+$, 416[M-3CO]$^+$, 388[M-4CO]$^+$, 360, [M-5CO]$^+$, 332[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{20}H_{14}$ Co_2O_8 cal: 443.9454[M-2CO]$^+$, found 443.9457

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(3-methoxyphenyl)pent-4-en-2-yne)]dicobalt (Co-Co) (131)

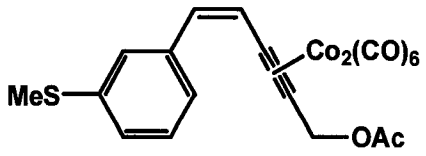


131

A solution of compound **120** (188.4 mg, 1.00 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **131** (391.5 mg, 1.23 mmol, 76% yield) as brown oil.

IR (neat, KBr): 2942, 2092, 2022, 1746, 1575, 1217, 1030 cm^{-1}. **^{1}H NMR**: δ 2.01 (3H, s), 3.80(3H, s), 4.51(2H, s), 6.61(1H, d, J=11.1), 6.70 (1H, s), 6.77(2H, m), 6.85(1H, dd, J=8.3, 2.5), 7.30(1H, t, J=7.9). **^{13}C NMR**: δ 199.1(br), 170.5, 159.6, 132.0, 129.6, 127.8, 120.6, 114.2, 112.9, 91.3, 83.2, 64.7, 55.2, 20.3. **MS (EI, m/z):** 488$[M-CO]^+$, 460$[M-2CO]^+$, 432$[M-3CO]^+$, 404$[M-4CO]^+$, 376$[M-5CO]^+$, 348$[M-6CO]^+$. **HRMS (EI, m/z)** for $C_{20}H_{14}Co_2O_9$ cal: 459.9403$[M-CO]^+$, found 459.9391

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(3-methylthiophenyl)pent-4-en-2-yne)]dicobalt (Co-Co) (132)



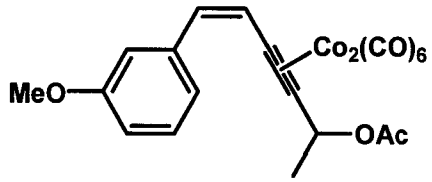
132

A solution of compound **121** (78 mg, 0.38 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **132** (168 mg, 0.31 mmol, 86% yield) as a brown oil.

IR (neat, KBr): 2925, 2092, 2022, 1746, 1373 cm^{-1}. **^{1}H NMR**: δ 2.03(3H, s), 2.49(3H, s), 4.55(2H, s), 6.64(1H, d, J=10.8), 6.78 (1H, d, J=10.9), 6.97(1H, d,

J=7.0), 7.07(1H, s), 7.21(1H, d, J=8.0), 7.30(1H, t, J=7.8). **^{13}C NMR**: δ 199.1(br), 170.4, 139.1, 138.2, 131.5, 128.9, 128.2, 126.1,125.5, 124.8, 91.3, 82.9, 64.6, 20.3, 15.5. **MS (EI, m/z):** 504[M-CO]$^+$, 476[M-2CO]$^+$, 448[M-3CO]$^+$, 420[M-4CO]$^+$, 392[M-5CO]$^+$, 364[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{20}H_{14}Co_2O_8S$ cal: 363.9452[M-6CO]$^+$, found 363.9400.

Hexacarbonyl[μ-η^4-(2-acetoxy-5-(3-methoxyphenyl)hex-5-en-3-yne)]dicobalt (Co-Co) (133)

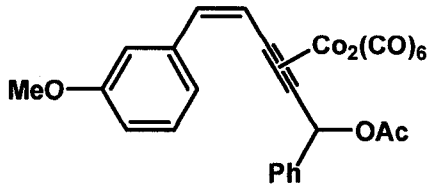


133

A solution of compound **122** (123 mg, 0.61 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **133** (221 mg, 0.42 mmol, 70% yield) as a brown oil.

IR (neat, KBr): 2091, 2051, 2022, 1741,1574, 1234, 1050 cm^{-1}. **^{1}H NMR**: δ 0.92(3H, d, J=6.1), 2.04(3H, s), 3.84(3H, s), 5.88(1H, q, J=5.9), 6.59(1H,d, J=11.3), 6.77 (1H, d, J=11.0), 6.87(3H, m), 7.34(1H, m). **^{13}C NMR**: δ 199.2(br), 170.0, 159.8, 138.5, 132.2, 129.6, 127.2, 120.9, 113.9, 113.4, 98.4, 83.2, 71.3, 55.2, 22.5, 20.6 **MS (EI, m/z):** 474[M-2CO]$^+$, 446[M-3CO]$^+$, 418[M-4CO]$^+$, 390[M-5CO]$^+$, 362. [M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{21}H_{16}Co_2O_9$ cal: 445.9593[M-3CO]$^+$, found 445.9611.

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(3-methoxyphenyl)-1-phenyl-pent-4-en-2-yne)]dicobalt (Co-Co) (134)

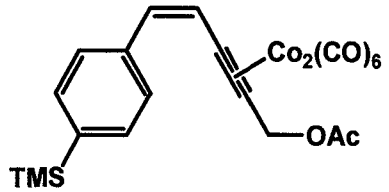


134

A solution of compound **123** (111 mg, 0.42 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **134** (200.4 mg, 0.34 mmol, 80% yield) as a brown oil.

IR (neat, KBr): 2091, 2054, 1748, 1371 cm^{-1}. **^{1}H NMR**: δ 2.17(3H, s), 3.81(3H, s), 6.61(1H, d, J=11.6), 6.81(3H, m), 6.91 (1H, s), 6.99(1H, s), 7.18(2H, d, J=6.8), 7.30(4H, m). **^{13}C NMR**: δ 198.6(br), 169.6, 159.8, 140.8, 138.2, 133.8, 129.5, 128.5, 128.2, 126.9, 125.7, 121.3, 114.3, 113.1, 99.9, 83.9, 75.6, 55.2, 20.7. **MS (EI, m/z)**: 508[M-3CO]$^+$, 424[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{26}H_{18}Co_2O_9$ cal: 507.9767[M-3CO]$^+$, found 507.9739

Hexacarbonyl[μ-η^4-(1-Acetoxy-5-(4-trimethylsilylphenyl)pent-4-en-2-yne)]dicobalt (Co-Co) (135)

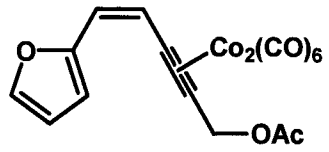


135

A solution of compound **124** (156 mg, 0.68 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **135** (301 mg, 0.54 mmol, 80% yield) as brown oil.

IR (neat, KBr): 2957, 2092, 2052, 1748, 1373, 1217, 1030 cm^{-1}. **^{1}H NMR**: δ0.91(9H, s), 2.03 (3H, s), 4.52(2H, s), 6.65(1H, d, J=11.1), 6.83 (1H,d, J=11.1), 7.21(2H, d, J=7.7), 7.56 (2H, d, J=7.7). **^{13}C NMR**: δ199.1(br), 170.3, 140.4, 138.0, 133.4, 132.4, 127.7, 127.6, 91.4, 83.4, 67.4, 20.2, -1.3. **MS (EI, m/z):** 498[M-2CO]$^+$, 474[M-3CO]$^+$, 446[M-4CO]$^+$, 418[M-5CO]$^+$, 390[M-6CO]$^+$.

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(2-furyl)pent-4-en-2-yne)] dicobalt (Co-Co) (136)



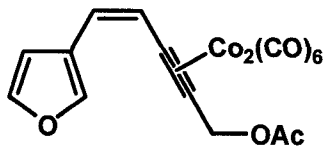
136

A solution of compound **125** (64 mg, 0.43 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **136** (146 mg, 0.31 mmol, 71% yield) as brown oil.

IR (neat, KBr): 2090, 2021, 1744, 1606, 1374, 1217, 1020 cm^{-1}. **^{1}H NMR**: δ 2.15 (3H, s), 5.50(2H, s), 6.32(1H, d, J=11.9), 6.47 (3H, m), 7.56(1H, s). **^{13}C NMR**: δ 199.2(br), 170.9, 152.3, 143.4, 122.8, 117.3, 112.8, 112.0, 92.5, 84.3, 66.0, 20.5. **MS (EI, m/z)**: 448[M-CO]$^+$, 420[M-2CO]$^+$, 392[M-3CO]$^+$, 364[M-4CO]$^+$,

336[M-5CO]$^+$, 308[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{17}H_{10}Co_2O_9$ cal: 419.9090[M-2CO]$^+$, found 419.9059.

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(3-furyl)pent-4-en-2-yne)]dicobalt (Co-Co) (137)

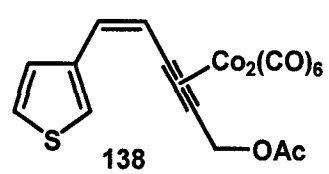


137

A solution of compound **126** (85.2 mg, 0.58 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **137** (192mg, 0.40mmol, 70% yield) as a brown oil.

IR (neat, KBr): 2361, 2338, 2093, 2023, 1747, 1608. **^{1}H NMR**: δ 2.09 (3H, s), 4.94(2H, s), 6.36(1H, s), 6.48(1H, d, J=11.0), 6.60(1H, d, J=11.0), 7.39(1H, s), 7.48(1H, d, J=1.48). **^{13}C NMR**: δ 199.1(br), 170.5, 143.4, 140.6, 128.5, 122.5, 121.9, 111.2, 91.1, 83.2, 64.8, 20.3. **MS (EI, m/z):** 448[M-CO]$^+$, 420[M-2CO]$^+$, 392[M-3CO]$^+$, 364[M-4CO]$^+$, 336[M-5CO]$^+$, 308[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{17}H_{10}Co_2O_9$ cal: 419.9090[M-2CO]$^+$, found 419.9078.

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(3-thienyl)pent-4-en-2-yne)]dicobalt (Co-Co) (138)

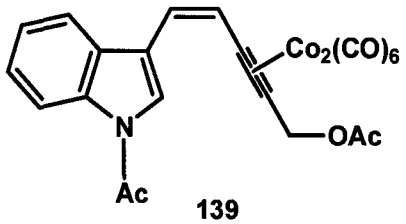


138

A solution of compound **127** (62 mg, 0.38mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to afford pure product **138** (154mg, 0.31mmol, 81% yield) as a brown oil.

IR (neat, KBr): 3425, 3013, 2956, 2923, 2092, 2022, 1746 cm^{-1}.**^{1}H NMR**: δ 2.07(3H, s), 4.73(2H, s), 6.62(1H, d, J=11.0),6.67(1H, d, J=11.0), 6.98(1H, d, J=4.3), 7.13(1H, s). 7.38(1H, s). **^{13}C NMR**: δ 199.3(br), 170.5, 138.2, 128.3, 128.2, 126.8, 126.2, 123.4, 91.4, 83.3, 64.5, 20.3. **MS (EI, m/z)**: 464$[M-CO]^+$, 436$[M-2CO]^+$, 408$[M-3CO]^+$, 380$[M-4CO]^+$, 352$[M-5CO]^+$, 324$[M-6CO]^+$. **HRMS (EI, m/z)** for $C_{17}H_{10}Co_2O_8S$ cal: 435.8862$[M-2CO]^+$, found: 435.8853.

Hexacarbonyl[μ-η^4-(1-acetoxy-5-(1-acetylindol-3-yl)-pent-4-en-2-yne)]dicobalt (Co-Co) (139)



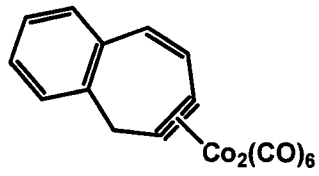
139

A solution of compound **128** (33 mg, 0.14 mmol) in CH_2Cl_2 was subject to **procedure C** to yield a crude product. The crude compound was purified by flash chromatography (5:1 petroleum ether: diethyl ether) to afford pure product **139** (57 mg, 0.10 mmol, 72% yield) as a brown oil.

IR (neat, KBr): 2092, 2052, 2024, 1744, 1714 cm^{-1}. **^{1}H NMR**: δ 1.96 (3H, s), 2.68(3H, s), 4.57(2H, s), 6.71(1H, d, J=10.7), 6.84(1H, d, J=10.7), 7.31 (2H, m), 7.47(2H, m), 8.46(1H, s). **^{13}C NMR**: δ 199.0(br), 170.5, 168.5, 135.4, 130.1,

126.0, 124.0, 122.9, 119.3, 119.2, 116.8, 91.0, 82.8, 64.3, 23.8, 20.2. **MS (EI, m/z)**: 458[M-CO]$^+$, 430[M-2CO]$^+$, 402[M-3CO]$^+$, 374[M-4CO]$^+$, 346[M-5CO]$^+$, 318[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{23}H_{15}NCo_2O_9$ cal: 482.9563[M-3CO]$^+$, found 482.9554

Hexacarbonyl[μ-η^4-(5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co)(140)

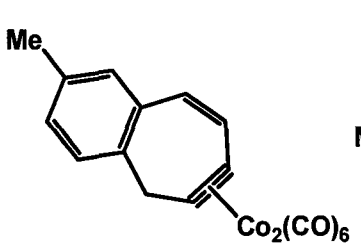


140

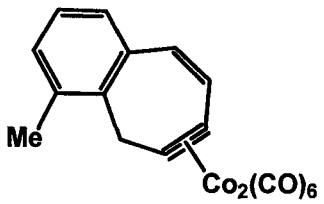
To a stirred ice cold solution of compound **129** (24.7 mg, 0.05 mmol) in CH_2Cl_2 (5 mL), was added $BF_3.OEt_2$ (21.3 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 3.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain sequentially product **140** (10.5 mg, 49%) as a brown oil and recovered starting material (2.2mg, 9%).

IR (neat, KBr): 2929, 2362, 2091, 2021,1574 cm^{-1}.^{1}**H NMR**: δ 4.18 (2H, s), 6.77(1H, d, J=10.1), 6.93(1H, d, J=10.1), 7.22(4H, m). ^{13}**C NMR:** δ 199.3(br), 137.5, 137.3, 133.1, 132.5, 129.4, 128.9, 128.8, 126.9, 102.3, 86.5, 40.8. **MS (EI, m/z)**: 426[M]$^+$, 398[M-CO]$^+$, 370[M-2CO]$^+$, 342[M-3CO]$^+$, 314[M-4CO]$^+$, 286[M-5CO]$^+$, 258[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{17}H_8Co_2O_6$ cal: 426.9063[M+H]$^+$, found 426.9069.

Hexacarbonyl[μ-η^4-(2-methyl-5H-benzocycloheptenyne)]dicobalt (Co-Co) (141a) and Hexacarbonyl[μ-η^4-(4-methyl-5H-benzocycloheptenyne)]dicobalt (Co-Co) (141b)



141a

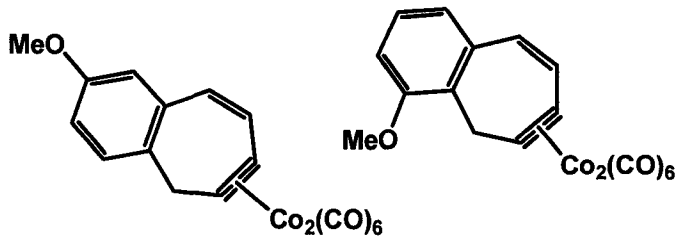


141b

To a stirred ice cold solution of compound **130** (44.5 mg, 0.09 mmol) in CH_2Cl_2 (20 mL) solution, was added $BF_3.OEt_2$ (38 mg, 0.27 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 1.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain a mixture of product **141a & 141b** (27 mg, 68% yield, 3:1) as a brown oil.

IR (neat, KBr): 3014, 2858, 2090, 2053, 2021, 1557 cm^{-1}. **^{1}H NMR**: **141a**: δ 2.31 (3H, s), 4.14(2H, s), 6.72(1H, d, J=10.1), 6.90(1H, d, J=10.1), 7.00(1H, s), 7.07(1H, d, J=7.9), 7.15(1H, d, J=7.6). **141b**: δ 2.51(3H, s), 4.10(2H, s), 6.82(1H, d, J=10.0), 6.93(1H, d, J=10.0), 7.03(1H, m), 7.10(1H, m), 7.17(1H, m). **^{13}C NMR: 141a** δ 199.4(br), 137.3, 136.4, 134.5, 133.2, 129.6, 129.4, 128.5, 102.5, 86.9, 40.4, 20.7. **141b** (incomplete) 133.8, 130.7, 130.4, 128.8, 126.3, 34.2, 21.1. **MS (EI, m/z)**: 440.0[M]$^+$, 412[M-CO]$^+$, 384[M-2CO]$^+$, 356[M$^+$-3CO], 328[M-4CO]$^+$, 300[M-5CO]$^+$, 272[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{18}H_{10}Co_2O_6$ cal: 439.9141 found 439.9137

Hexacarbonyl[μ-η^4-(2-methoxy-5H-benzocycloheptenyne)]dicobalt (Co-Co) (142a) and Hexacarbonyl[μ-η^4-(4-methoxy-5H-benzocycloheptenyne)] dicobalt (Co-Co) (142b)



142a **142b**

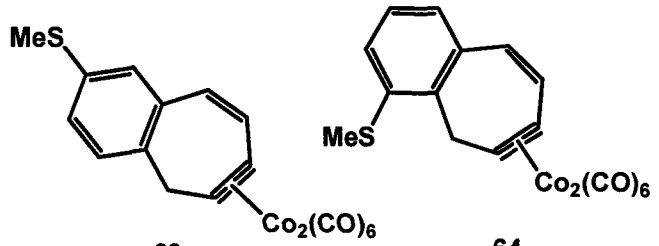
To a stirred ice cold solution of compound **131** (25.8 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) solution, was added $BF_3.OEt_2$ (21.3 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 0.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain sequentially products **142b** & **142a** (10.5 mg, 53%yield, 4.9: 1) as brown oils.

142a: IR (neat, KBr), 3014, 2956, 2837, 2090, 2050, 2020, 1604 cm^{-1}. **^{1}H NMR:** δ 3.77(3H, s), 4.10(2H, s), 6.68(1H, d, J=10.1), 6.71(1H, s), 6.79(1H, d, J=8.3), 6.92(1H, d, J=10.1), 7.16(1H, d, J=8.3) **^{13}C NMR:** δ 199.3(br), 158.3, 138.6, 132.8, 130.5, 130.0, 129.3, 117.7, 113.9, 102.9, 86.6, 55.3, 39.9. **MS (EI, m/z):** 456[M]$^+$, 428[M-CO]$^+$, 400[M-2CO]$^+$, 372, [M-2CO]$^+$, 344[M-4CO]$^+$, 316[M-5CO]$^+$, 288[M-6CO]$^+$. **HRMS (EI, m/z) for** $C_{18}H_{10}Co_2O_7$ cal: 455.9090, found: 455.9051.

142b: IR (neat, KBr): 3008, 2958, 2923, 2851, 2090, 2050, 2020, 1618, 1596.**^{1}H NMR:** δ 3.89 (3H, s), 4.29(2H, s), 6.74(1H, d, J=10.1), 6.80(1H, d, J=7.7), 6.87(1H, d, J=7.7), 6.92(1H, d, J=10.1), 7.15(1H, t, J=7.9). **^{13}C NMR**: δ 199.6(br),

156.9, 139.1, 133.3, 129.0, 127.1, 126.4, 125.2, 111.3, 103.8, 86.6, 56.3, 30.0. **MS (EI, m/z):** 456[M]$^+$, 428[M-CO]$^+$, 400[M-2CO]$^+$, 372[M-2CO]$^+$, 344[M-4CO]$^+$, 316[M-5CO]$^+$, 288[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{18}H_{10}Co_2O_7$ cal: 455.9090[M]$^+$, found 455.9089.

Hexacarbonyl[μ-η^4-(2-methylthio-5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co) (143a) and Hexacarbonyl[μ-η^4-(4-Methylthio-5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co) (143b)



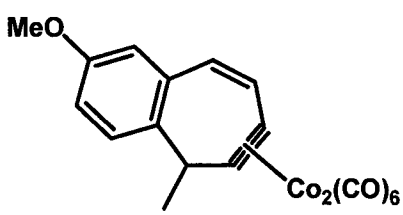
63 64

To a stirred ice cold solution of compound **131** (38.5 mg, 0.07 mmol) in CH_2Cl_2 (1 mL) solution, was added $BF_3.OEt_2$ (32.3 mg, 0.23 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (20:1 petroleum ether: diethyl ether) to obtain a mixture of product **143a** and **143b** (5.5 mg, 18% yield, 4:1) as brown oil.

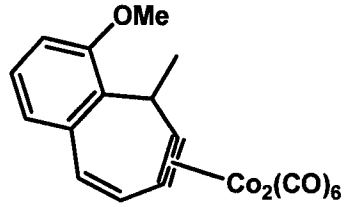
IR (neat, KBr): 3450, 2924, 2090, 2053, 2024, 1638, 1458 cm^{-1}. **^{1}H NMR: 143a** δ 2.46(3H, s), 4.14(2H, s), 6.70(1H, d, J=10.2), 6.96(1H, d, J =10.2), 7.09(1H, s), 7.16(2H, m) **143b**: (incomplete) 2.50 (3H, s), 4.36(2H, s), 6.79(1H, d, J=10.0), 6.99(1H, d, J=10.0), 7.03 (1H, d, J=7.6). **^{13}C NMR: 143a** δ 199.3(br), 138.1, 137.1, 134.5, 132.5, 130.8, 129.9, 129.6, 127.2 102.0, 86.3, 40.3, 22.6.

MS (EI, m/z): 472[M]$^+$, 444[M-2CO]$^+$, 416[M-3CO]$^+$, 388[M-4CO]$^+$, 360[M-5CO]$^+$, 332[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{18}H_{10}Co_2O_6S$ cal: 303.9167[M-6CO]+, found 303.9179.

Hexacarbonyl[μ-η^4-(2-methoxy-5-methyl-5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co) (144a) and Hexacarbonyl[μ-η^4-(4-methoxy-5-methyl-5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co) (144b)



144a



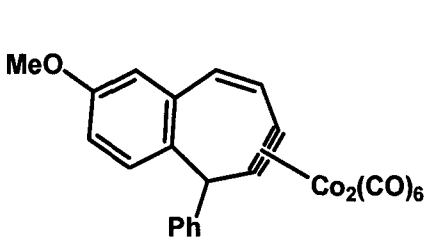
144b

To a stirred ice cold solution of compound **133** (85.9 mg, 0.16 mmol) in CH_2Cl_2 (16 mL), was added $BF_3.OEt_2$ (68.4 mg, 0.49 mmol) in CH_2Cl_2 (2 mL) over 10 minutes. After stirring for 1.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain a mixture of product **144a** and **144b** (58.2 mg, 77% yield, 7:1) as a brown oil.

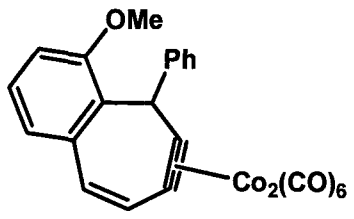
IR (neat, KBr): 2090, 2050, 2020, 1604, 1556 cm^{-1}. **^{1}H NMR**: **144a** δ. 1.51(3H, d, J=6.7), 3.80(3H, s), 4.17 (1H, q, J=7.1), 6.73(1H, d, J=10.5), 6.96(1H, d, J=9.9), 6.76(1H, s), 6.85(1H, dd, J=8.4, 2.5), 7.24(1H, d, J=8.5). **144b** (Incomplete): 1.29(3H,d, J=7.2), 3.90(3H, s), 5.27(1H, q, J=7.3), 6.90(2H, m), 7.16 (1H, t, J=8.0). **^{13}C NMR: 144a** δ. 199.6(br), 158.1, 137.6, 135.6, 133.0,

129.2, 128.9, 118.0, 114.0, 109.2, 84.8, 55.2, 43.7, 22.1. **144b** (incomplete). 133.3, 129.0, 43.7, 24.6. **MS (EI, m/z)**: 470[M^+], 442[M-CO]$^+$, 414[M-2CO]$^+$, 386[M-2CO]$^+$, 358[M-4CO]$^+$, 330[M-5CO]$^+$, 302[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{19}H_{12}Co_2O_7$ cal: 441.9298[M-CO]$^+$, found 441.9255.

Hexacarbonyl[μ-η^4-(2-methoxy-5-phenyl-5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co) (145a) and hexacarbonyl[μ-η^4-(4-methoxy-5-phenyl-5H-benzocyclohept-8-en-6-yne)]dicobalt (Co-Co) (145b)



145a



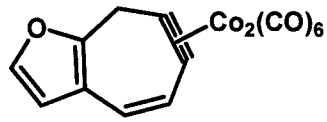
145b

To a stirred ice cold solution of compound **134** (66.8 mg, 0.11 mmol) in CH_2Cl_2 (11 mL), was added $BF_3.OEt_2$ (48.1 mg, 0.34 mmol) in CH_2Cl_2 (2 mL) over 10 minutes. After stirring for 1.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain a mixture of product **145a& 145b** (54.3 mg, 90% yield, 12.5:1)) as brown oil.

IR (neat, KBr): 2090, 2052, 2022, 1602, 1556 cm^{-1}. **^{1}H NMR: 145a:** δ 3.88(3H, s), 5.35 (1H, s), 6.77(1H, dd, J=8.6, 2.6), 6.82(1H, s), 6.83(1H, m), 7.01(1H, d, J=10.1), 7.09(1H, d, J=8.5), 7.23(1H, m), 7.29(2H, m), 7.35(2H, m). **145b** (incomplete) δ 3.80(3H, s), 5.30(2H, s). **^{13}C NMR:145a** δ199.4(br), 158.3,

144.4, 144.4, 138.3, 133.5, 133.1, 131.3, 129.6, 128.6, 127.0, 118.4, 114.2, 107.1, 84.8, 55.4, 55.3. **MS (EI, m/z))**: 504[M-CO]$^+$, 476[M-2CO]$^+$, 448[M-3CO]$^+$, 420[M-4CO]$^+$, 392[M-5CO]$^+$, 364[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{24}H_{14}Co_2O_7$ cal: 503.9454[M-CO]$^+$, found 503.9437.

Hexacarbonyl[μ-η^4-(8H-cyclohept-4-en-6-yn[b]furan)]dicobalt (Co-Co)(146)

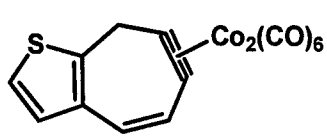


146

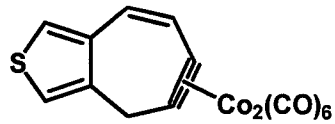
To a stirred ice cold solution of compound **137** (24.7 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) was added $BF_3.OEt_2$ (22.1 mg, 0.16 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 0.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtain product **146** (16.9 mg, 78% yield) as a brown oil.

IR (neat, KBr): 2092, 2051, 2020. **^{1}H NMR**: δ. 4.47 (2H, s), 6.31(1H, s), 6.39(1H, d, J=9.6), 6.57(1H, d, J=9.6), 7.30(1H, s). **^{13}C NMR:** δ 199.3(br), 148.8, 140.8, 125.1, 124.1, 120.5, 113.3, 92.2, 86.6 34.0. **MS (EI, m/z):** 416[M]$^+$, 388[M-CO]$^+$, 360[M-2CO]$^+$, 332[M-3CO]$^+$, 304[M-4CO]$^+$, 276[M-5CO]$^+$, 248[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{15}H_6Co_2O_7$ cal: 415.8777[M]$^+$, found 415.8752.

Hexacarbonyl[μ-η^4-(8H-cyclohept-4-en-6-yn[b]thiophene)] dicobalt (Co-Co) (147a) and Hexacarbonyl[μ-η^4-(4H-cyclohept-7-en-5-yn[c]thiophene)] dicobalt (Co-Co)(147b)



147a

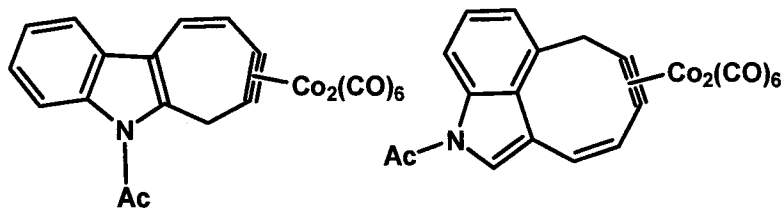


147b

To a stirred ice cold solution of compound **138** (30.1 mg, 0.06 mmol) in CH_2Cl_2 (1.2 mL) solution, was added $BF_3.OEt_2$ (26.0 mg, 0.18 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 0.5 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtain an inseparable mixture of product **147a** and **147b** (22.1 mg, 83% yield, 5:1) as brown oil.

IR (neat, KBr): 2926, 2856, 2092, 2055, 2024, 1699, 1650, 1540 cm^{-1}. **^{1}H NMR: 147a** δ 4.45 (2H, s), 6.69(2H, dd, J=19.7, 9.6), 6.88(1H, d, J=8.7), 7.08(1H, d, J=8.8). **147b: (in CD_3CN):** δ 4.34(2H, s), 6.66(1H, d, J=9.9), 6.80(1H, d, J=9.7), 7.20(1H, s), 7.38(1H, s) **^{13}C NMR: 147a** δ 199.1(br), 136.8, 136.7, 132.0, 126.4, 126.2, 122.0, 97.6, 86.8, 34.6. **147b** (incomplete) 128.7, 126.9, 124.8, 35.5, **MS (EI, m/z):** 432[M]$^+$, 404[M-CO]$^+$, 376[M-2CO]$^+$, 348[M-3CO]$^+$, 320[M-4CO]$^+$, 292[M-5CO]$^+$, 264[M-6CO]$^+$. **HRMS (EI, m/z) for** $C_{15}H_6Co_2O_6S$ cal: 403.8575 [M-CO]$^+$, found 403.8554

Hexacarbonyl[μ-η^4-(5-acetyl-5,6-dihydro-7,8-dehydrocyclohepta[b]indole)] dicobalt (Co-Co) (148a) and hexacarbonyl[μ-η^4-(2-acetyl-2,6-dihydro-8,9-dehydro-2-azacycloocta[cd]indene)]dicobalt (Co-Co) (148b)



148a **148b**

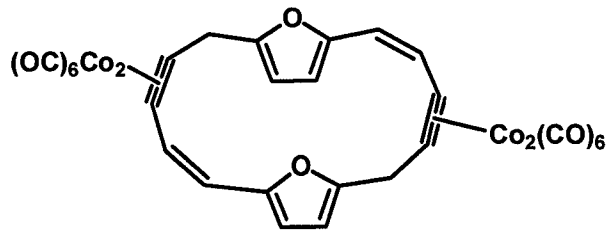
To a stirred ice cold solution of compound **139** (23.0 mg, 0.04 mmol) in CH_2Cl_2 (4 mL) solution, was added $BF_3.OEt_2$ (17.5 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 2 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (10:1 petroleum ether: diethyl ether) to obtain sequentially product **148a** (7.8 mg, 38% yield) and product **148b**(9.7 mg, 47% yield) as brown oils.

148a. IR (neat, KBr): 3454, 2091, 2050, 2018,1710,1638 cm^{-1}. **^{1}H NMR**: δ 2.88(3H, s), 4.99 (2H, s), 6.79(1H, d, J=9.6), 6.92(1H, d, J=9.5), 7.32(2H, m), 7.66(2H, m). **^{13}C NMR**: δ 199.2(br), 171.2, 135.2, 134.8, 130.1, 126.2, 124.6, 123.2, 121.9, 118.7, 118.4, 113.7, 95.0, 85.8, 35.6, 28.1. **MS (EI,m/z)**: 479[M-CO]$^+$, 451[M-2CO]$^+$, 423[M-3CO]$^+$, 395[M-4CO]$^+$, 367[M-5CO]$^+$, 339[M-6CO]$^+$. **HRMS (EI, m/z)** for $C_{21}H_{11}Co_2NO_7$ cal: 478.9250[M-CO]$^+$, found 478.9232.

148b. IR (neat, KBr), 3466, 2927, 2089, 2049, 2014, 1717,1593 cm^{-1}. **^{1}H NMR**: δ. 2.65(3H, s), 4.49 (2H, s), 6.61(2H, dd, J=23, 11.1), 7.29(2H, d, J=4.8),

7.51(1H, m). 8.53(1H, s) **^{13}C NMR**: 199.3(br), 168.1, 138.3, 134.7, 128.7, 126.4, 126.1, 125.7, 125.2, 124.4, 121.0, 116.0, 99.0, 89.1, 41.6, 24.2. **MS (EI, m/z)**: $[M-CO]^+$ 479, $[M-2CO]^+$ 451, $[M-3CO]^+$ 423, $[M-4CO]^+$ 395, $[M-5CO]^+$ 367, $[M-6CO]^+$ 339. **HRMS (EI, m/z)** for $C_{21}H_{11}Co_2NO_7$ cal: $[M-2CO]^+$450.9301, found 450.9283.

Compound 149

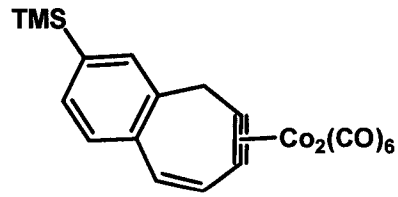


149

To a stirred ice cold solution of compound **125** (26.5 mg, 0.06 mmol) in CH_2Cl_2 (1.2 mL) was added $BF_3.OEt_2$ (23.7 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. After stirring for 4 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain product **149** (7.0 mg, 30% yield) as a brown oil.

IR (neat, KBr) 3442, 2924, 2853, 2089, 2052, 2021, 1641, 1463. **^{1}H NMR**: δ. 4.25 (4H, s), 6.23(4H, s), 6.63(2H, d, J=15.0), 7.83(2H, d, J=15.0). **MS (EI, m/z)**: 804$[M-CO]^+$, 776$[M-2CO]^+$, 748$[M-3CO]^+$, 720$[M-4CO]^+$, 692$[M-5CO]^+$, 664$[M-6CO]^+$, 636$[M-7CO]^+$.

Hexacarbonyl[μ-η^4-(3-trimethylsilyl-5H-benzocyclohept-8en-6yne)]dicobalt (Co-Co) (150)

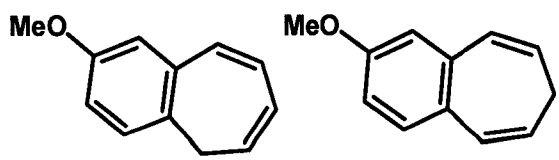


150

To a stirred ice cold solution of compound **135** (94.8 mg, 0.17 mmol) in dichloromethane (9 mL) solution, was added $BF_3.OEt_2$ (74.2 mg, 0.51 mmol) in CH_2Cl_2 (1 mL) over 10 minutes. . After stirring for 6 hours, saturated sodium bicarbonate solution was added. After a conventional work up, the crude product was purified by flash chromatography (100% petroleum ether) to obtain sequentially product **150** (47.5 mg, 58% yield) as a brown oil and recovered starting material (11.4 mg, 12% yield).

IR (neat, KBr): 2957, 2360, 2091, 2052, 2022 cm^{-1}. **^{1}H NMR**: δ 0.28(9H, s), 4.20 (2H, s), 6.76(1H, d, J=10.1), 6.94(1H, d, J=10.1), 7.16(1H, d, J=7.5) 7.36(1H, s), 7.37(1H, d, J=6.2). **^{13}C NMR**: δ 199.4(br), 142.0, 137.7, 136.3, 134.2, 133.2, 131.9, 131.7, 129.0, 102.4, 86.6, 40.9, -1.2. **MS (EI, m/z)**: 498$[M]^+$, 470$[M\text{-}CO]^+$, 442$[M\text{-}2CO]^+$, 414$[M\text{-}3CO]^+$, 386$[M\text{-}4CO]^+$, 358$[M\text{-}5CO]^+$, 330$[M\text{-}6CO]^+$. **HRMS (EI, m/z)** for $C_{20}H_{16}Co_2O_6Si$ cal: 469.9431$[M\text{-}CO]^+$, found 469.9434.

2-Methoxy-5H-benzocycloheptene (151a) and 2-methoxy-7H-benzocycloheptene (151b)



151a **151b**

To a solution of compound **142a**(103 mg, 0.22 mmol) in benzene (50 mL) was added Bu_3SnH (989 mg, 3.3 mmol), the mixtrue was heated to 52 ^0C and stirred for 3 h. After cooling down, the reaction mixture was filtered through a plug of Celite ®. Removal the solvent under reduced pressure. The crude product was purified by Prep TLC to obtain the inseparable mixture of compound **151a** and compound **151b** (21.2 mg, 56% yield; 3:1) as yellow oil

IR (neat, KBr) 3448, 3023, 2926, 2853, 1604, 1559, 1498, 1257. **^1H NMR**: **151a** δ. 3.01(2H, d, J=6.8), 3.81(3H, s), 5.82(1H, m), 6.01(1H, dd, J=11.5, 5.4), 6.47(1H, dd, J=11.5, 5.4,), 6.85(1H, d, J=2.6), 6.92(1H, dd, J=8.4, 2.6,), 7.03(1H, d, J=11.6), 7.08(1H, d, J=8.4) **151b**: (incomplete) 2.79(2H, t, J=5.2), 3.80(3H, s), 5.92(1H, dt, J=5.5, 12.2), 6.36(1H, dt, J=12.2, 1.85), 6.67 (1H, dd, J=8.3, 2.9), 6.71(1H, d, J=2.7), 7.01(1H, d, J=8.3). **^{13}C NMR**: **151a**: 157.5, 137.0, 133.3, 129.0, 128.4, 127.9, 125.7, 115,1, 112.1, 55.3, 33.6. **151b**: 157.8, 137.2, 134.2, 132.8, 129.9, 129.7, 129.5, 116.1, 111.8, 55.2, 35.1. **MS (EI m/z):** 172. **HRMS(EI, m/z)** cal: $[M-H]^+$171.0810, found 171.0819.

References

1. Melikyan, G. G.; Nicholas, K.M.; *Modern Acetylene Chemistry*, Strong, P.J.; Diederich, F. Eds. VCH press, NY, **1995**, Ch. 4, 99.
2. Went, M. J. Adv. Organomet. Chem. **1997**, *41*, 69.
3. Nicholas, K. M.; Petitt, R. *Tetrahedron Lett.* **1971,** 3475
4. Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207.
5. Connor, R. E.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45.
6. Gruselle, M.; Cordier, C.; Salmain, M.; El Amouri, H.; Guerin, C.; Vaissermann, J.; Jaouen, G. *Organometallics* **1990**, *9*, 2993.
7. Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, 268, C23.
8. Edidin, R. T.; Norton, J.; Mislow, K. *Organometallics* **1982**, *1*, 561.
9. Schreiber, S.L.; Klimas, M.T.; Sammakia, S. *J. Am. Chem. Soc.* **1987**, *109,* 5749.
10. Melikyan, G. G.; Bright, S.; Monroe, T.; Hardcastle, K. I.; Ciurash, J. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*,161.
11. Kuhn, O.; Rau, D.; Mayr, H. *J. Am. Chem. Soc.***1998**, *120*, 900.
12. Vizniowski, C. S.; Green J. R.; Breen, T. L.; Dalacu, A. V; *J. Org. Chem.* **1995**, *60*, 7496.
13. Review of Nicholas reaction: Teobald, B.T. *Tetrahedron* **2002**, *58*, 4133
14. Nicholas, K.M.; Pettit, R. *J. Organomet. Chem.* **1972**, *44*, C21. 67.
15. Caffyn, A.; Nicholas, J. M. In Comprehensive Organometallic Chemistry II; Abel, E. W.; Stone, F. G. A.; Wilkinson, G.; Hegedus, L. S.; Ed.,Pergamon Oxford, **1995**, Vol. 12, Ch. 7.1, 685.

16. Green, J.R. *Curr. Org. Chem.* **2001**, *5*, 809.

17. Palazon, J. M.; Martin, V. S. *Tetrahedron Lett.* **1995**, *36*, 3549

18. Mukai,c.; Sugimoto,Y.; Ikeda,Y.; Hanaoka,M. *J. Chem. Soc. Chem. Commun*. **1994**, 1161.

19. Mukai,C.; Sugimoto,Y.; Ikeda,Y.; Hanaoka, M *Tetrahedron Lett*. **1994**, *35*, 2179.

20. Mukai, C.; Sugimoto, Y; Ikeda,Y.; Hanaoka, M. *Tetrahedron*, **1998**, *54*, 823.

21. Grove D. D.; Miskevich, F.; Smith, C. C; Corte, J. R. *Tetrahedron Lett.*, **1990**, *31*, 6277;

22. Grove D. D.; Corte, J. R.; Spencer, R. P.; Pauly; M. E.; Rath, N. P.; *J. Chem. Soc. Chem.Commun.*, **1994**, 49.

23. Muehdldorf, A. V.; Guzmanperez, A.; Kludge, A. F. *Tetrahedron Lett.* **1994**, *35*, 8755.

24. LeBrazidec, J. Y.; Kocienski, P. J.; Connolly, J. D.; Muir, K. W. *J. Chem. Soc.,Perkin Trans. 1*, **1998**, 2475.

25. Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3129.

26. Tanino, K.; Shimizu, T.; Miyama, M.; Kuwajima, I. *J. Am. Chem. Soc*. **2000**, *122*, 6116.

27. Isobe, M.; Nishizawa, R.; Hosokawa, S.; Nishizawa, T. *Chem.Commun.* **1998**, 2665.

28. Yenjai, C.; Isobe, M. *Tetrahedron* **1998**, *54*, 2509.

29. Isobe, M.; Yenjai, C.;Tanaka, S. *Synlett*,**1994**, 916.

30. Murata, M.; Legrand, A. M.; Ishibashi, Y.; Yasumoto, T. *J. Am. Chem. Soc.* **1989**, 111, 8929: *idem,ibid*, **1990**, *112*, 4380

31. a) Shibuya, S.; Isobe, M. *Synlett* **1998**, 373; b) Shibuya, S.; Isobe,M. *Tetrahedron* **1998**, *54*, 6677

32. Davies, J. E.; Hope-Weeks, L. J.; Mays, M. J.; Raithby, P. R. *Chem. Commun.* **2000**, 1411

33. Guo, R.; Green, J. R. *Synlett*, **2000,** 746.

34. Gibe, R.; Green, J. R. *Chem. Commun.* **2002**, 1750.

35. Kraft, M. E.; Cheung, Y. Y.; Wright, C.; Cali, R. *J. Org. Chem.* **1996**, *61*, 3912.

36. Nakamura, T.; Matsui, T.; Tanino, K.; Kuwajima, I. *J.Org.Chem.* **1997**, *62*, 3032.

37. Berge, J.; Claridge, S.; Mann, A.; Muller, C.; Tyrrell, E. *Tetrahedron Lett.* **1997**, *38*, 685.

38. Mann, A.; Muller, C.; Tyrrell, E.; *J. Chem. Soc. Perkin Trans. 1*, **1998**, 1427

39. Green, J. R. *Chem. Commun.* **1998**, 1751.

40. Patel, M. M.; Green, J. R. *Chem. Commun.* **1999**, 509.

41. Lu, Y.; Green, J. R. *Synlett,* **2001**, 243.

42. Green, J. R. *Synlett,* **2001**, 353.

43. Trinka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

44. Burlison, J. A.; Gray, J. M.; Young, D. G. J. *Tetrahedron Lett.* **2001**, *42*, 5363.

45. a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856. b) Grubbs, R. H. *J. Macromol. Sci.–Pure Appl. Chem.* **1994**, *A31*, 1829.

46. Iwasawa, N.; Satoh,H. *J. Am. Chem. Soc.* **1999**, *121*, 7951.

47. Khand, I. U.; Knox, G. R.; Pauson P. L.; Watts, W. E.; *J. Chem. Soc., Chem. Commun.* **1971**, 36.

48. Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1657.

49. Khand, I. U; Sugihara, T; Yamada, M.; Yamaguchi, M. Nishizawa, M. *Synlett*, **1999**, 771.

50. Pauson, P. L. *J. Chem. Res. (M.)*, **1977,** 168.

51. For recent review, see: a) Grotjahn, D. B. in Comprehensive Organometallic Chemistry II, Ed. Trost, B. M.; Abel, E.W.; Stone, F.G.A.; Wilkinson,G.; Hegedus, L. S.; Pergamon, New York, **1995**, Vol. 12, p. 741; b) Welker, M. E. *Curr. Org. Chem.,* **2001**, *5*, 785; c) Saito, S.; Yamamoto, Y.; *Chem.Rev.* **2000**, *100*, 2901; (d).Frühauf, H. W. *Chem. Rev.*, **1997**, *97*, 523; (*e*) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.*, **1996**, *96*, 49.

52. For recent examples, see: a) Co (I), Bruns, D.; Miura, H.; Vollhardt, K. P. C.; Stanger, A.; *Org. Lett*, **2003**, *5*, 549; b) Pd (0), Peña, D.; Pérez, D.;

Guitián, E.; Castedo, L. *Eur. J. Org. Chem.*, **2003**, 1238; c) Rh (I), Kinoshita, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.*, **2003**, *125*, 7784; d) Ni (0), Reinhard, S.; Soba, P.; Rominger ,F.; Blümel, J. *Adv. Synth. Catal.* **2003**, *345*, 589.

53. Sigman, M. S.; Fatland, A. W.; Eaton, B. E.; *J. Am. Chem. Soc.* **1998**, *120*, 5130.

54. Mohamed, A. B.; Green, J. R. *Chem Commun.* **2003**, 2936.

55. Recent review: Brocksom, T. J.; Nakamura, J.; Ferreira, M. L.; Brocksom, U.; *J. Braz. Chem. Soc.,* **2001**,*12*, 597.

56. Nicolaou, K. C.; Snyder, Scott A.; Montagnon, Tamsyn; Vassilikogiannakis, Georgios. *Angew Chem, Int. Ed.* **2002**, *41*, 1668.

57. Mach, K.; Antropiusova, H.; Petrusova, L.; Turecek, F.; Hanus, V. J. *Organomet. Chem.* **1985,** *289,* 331.

58. (a) Tom Dieck, H.; Diercks, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22,* 778; A*ngew. Chem. Suppl.* **1983,** 1138. (b) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Org. Chem.* **1968**, *33,* 3948. (c) Genet, J. P.; Ficini, J. *Tetrahedron Lett.* **1979**, 1499.

59. Matsuda, I.; Shibata, M.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1987**, *28*, 3361.

60. Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111,* 6432.

61. Hilt, G.; Smolko, K. I. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 2795.

62. Lautens, M.; Tam, J. W.; Edward, L G. *J. Org. Chem.* **1992**, *57*, 8.

63. Tallarico, J. A.; Randall, M. L.; Snapper, M. L. *J. Am. Chem. Soc.,* **1996**, *118,* 9196.

64. Iwasawa, N.; Sakurada, F.; Iwamoto, M., *Org. Lett.* **2000**, *2*, 871.

65. Kita,Y; Iio, K.; Kawaguchi, K; Fubuhisa, N.; Takeda, Y.; Ueno, H.; Okunako, R.; Higuchi, K.; Tsujino, T.; Fujioka, H.; Akai, S. *Chem. Eur. J.* **2000**, *6*, 3897.

66. Hamersma, W. J.; Synder, E.I. *J. Org. Chem.* **1965**, *30*, 3985.

67. a) Demirhan, F.; Gelling, A.; Irisi, S.; Jeffery, J.C.; Salek, S.N.; Senturk, O. S.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2765; b) Bennett, S.C., Jeffery, J.C., Went, M. J. *J. Chem. Soc., Dalton Trans.* **1994**, 3171.

68. For recent [4+2] examples: (a) Wang, B.; Cao, P.; Zhang, X. *Tetrahedron Lett,* **2000,** *41*, 8041; (b) Wender, P. A.; Smith, T. E. *Tetrahedron* **1998**, *54*, 1255; (c) Gilberson, S. R.; Hoge, G. S. *Tetrahedron Lett.* **1998**, *39*, 2075; (d) O'Mahony, D. J. R.; Belanger, D. B.; Livinghouse, T. *Synlett* **1998**, 443; (e) Gilberson, S. R.; Hoge, G. S.; Genov, D. G. *J. Org. Chem.* **1998**, *63*, 10077; (f) Kumar, K.; Jolly, R. S. *Tetrahedron Lett.* **1998**, *39*, 3047.

69. Wender, P.A.; Deschamps, N. M.; Gamber, G. G. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 1853.

70. Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

71. Obora, Y., Tsuji, Y., Kawamura, T. *J. Am. Chem. Soc.* **1993,** *115*,10414.

72. Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745.

73. Uenishi, J.; Kawahama, R.; Yonemitsu, O. *J.Org. Chem.* **1996**, *63*, 8965.

74. Taylor, R.; *Thiophene and Its Derivatives (The Chemistry of Heterocyclic Compounds*). Vol 44, Part II. Gronowitz, S. Ed. **1985**, John Wiley & Sons, Inc. 16.

75. Teranishi,K.; Hayashi, S.; Nakatshuka, S.; Goto, T; *Tetrahedron Lett.* **1994**, *35*, 8173.

76. a) Takai, S.; Ploypradith, P.; Hamajima, A.; Kira, K.; Isobe, M. *Synlett* **2002**, 588; b) Hosokawa, S.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 2609.

77. Smit, W.A.; Caple, R.; Smoliakova, I.P. *Chem. Rev.* **1994**, *94*, 2359.

78. Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

79. Patel, M.M. M.Sc. Thesis, University of Windsor, **1999**.

80. Euerby, M.; Waigh, R. *Synth. Commun.* **1981**, *11*, 849.

81. Yea, B.; Narutaa, Y. *Tetrahedron* **2003**, *59*, 3593.

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